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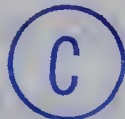
COMPUTER CALCULATION OF MULTICOMPONENT

VAPOR-LIQUID EQUILIBRIA AND ITS

APPLICATION TO THE DESIGN OF

DISTILLATION COLUMNS

BY



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A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Computer Calculation of Multicomponent Vapor-Liquid Equilibria and its Application to the Design of Distillation Columns" submitted by Antoine M. Hakim in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

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## ABSTRACT

The semi-empirical model for the calculation of vapor-liquid equilibrium presented by Prausnitz is evaluated. The Prausnitz model uses the Wilson equation as the source for the multicomponent liquid activity coefficients. The properties of the Wilson parameters and the interaction energies are investigated, and two optimization techniques are used to locate the Wilson or interaction energy parameters that will best predict the vapor-liquid equilibria in a system.

The Prausnitz equilibrium model is incorporated in a distillation routine which uses a tridiagonal matrix method to solve the material balance equations and the Muller method to calculate bubble-point temperatures. This distillation program is used to study and optimize the extractive distillation of the system MCH-toluene with phenol. The same program is used to simulate the Chemcell Ltd. distillation of acetone-methanol with water as the extractive agent. The simulation succeeds in duplicating the product purities. The program is then used to determine more optimal operating conditions for this industrial column.



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## I. INTRODUCTION

The sound design of equipment for separation operations necessitates the availability of reliable vapor-liquid equilibria.

Experimental data for binary vapor-liquid equilibria are often available, but experimental ternary equilibria are rare, and for systems with more than three components, laboratory data are practically non-existent. Thus, the value of a semi-theoretical model that could predict multicomponent vapor-liquid equilibria using information from binary equilibria only is obvious.

Several methods for the prediction of multicomponent equilibria are available. Carlson and Colburn and Wohl have presented excellent reviews of these methods. All of these, however, involve long and tedious calculations in their rigorous forms and the short cuts that have been used to speed their solution have led to a lack of accuracy.

The development of large-memory computers has encouraged the formulation and use of several semi-theoretical vapor-liquid equilibrium models which are applicable to wide ranges of components. Two such models are the Chao-Seader and the Prausnitz models, the latter based on the equation of Wilson. The Chao-Seader model is primarily designed to handle hydrocarbon mixtures, but it can also predict the equilibria for several non-condensable gases and boiling



point cuts of petroleum. The Prausnitz model predicts multicomponent equilibria using liquid activity coefficients obtained from Wilson's equation.

Orye and Prausnitz were the first to conclude that the thermodynamic model presented by Wilson did actually provide a sound model for prediction of multicomponent equilibria. Since this model appeared to handle polar components well, it was decided to study the possibilities it offered in the prediction of multicomponent vapor-liquid equilibria.

One objective of this work then is to achieve a better understanding of the Prausnitz model and test its ability to predict multicomponent equilibria for a wide range of systems. Another objective is to develop a computer routine which can be used for the reliable design of equipment for multicomponent distillation. The incorporation of the Prausnitz and the Chao-Seader models in such a routine would have special applications in the design of extractive distillation equipment.





## II - LITERATURE SURVEY

### 2.1 Determination of Vaporization Constants

A comprehensive review of the methods available for multicomponent equilibria prediction prior to 1946 is presented by Carlson and Colburn<sup>1</sup> and Wohl<sup>2</sup>. Since the development of high-speed digital computers, several models and data correlations designed for computer calculations are now available<sup>3,4,5,6</sup> the most notable being the Chao-Seader<sup>3</sup> and Prausnitz<sup>4</sup> correlations.

The Chao-Seader<sup>3</sup> correlation provides equilibrium ratios for hydrocarbons of various molecular structures, some common non-condensibles<sup>7</sup> ( $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{O}_2$ ), and heavier hydrocarbon fractions, all over wide pressure and temperature ranges.

A recent publication by Orye and Prausnitz<sup>4</sup> proposes a semi-empirical model for the calculation of vapor-liquid equilibria. The model is studied by Lyckman et al<sup>8</sup>, O'Connell et al<sup>9</sup>, and more comprehensively in a recently published nomograph<sup>10</sup>.

The Prausnitz model calculates independently the fugacity of the pure liquid and the fugacity coefficient of the vapor phase. A calculation of the latter at low system pressures is possible<sup>11</sup> through the use of the Pitzer and curl<sup>12</sup> model presented by Lewis and Randall<sup>13</sup>.



The liquid phase activity coefficients are calculated using the Wilson model<sup>14</sup>. This model uses the Flory<sup>15</sup> and Huggins<sup>16</sup> concept of athermal solutions whereby excess enthalpy is set to zero.

## 2.2 Determination of Enthalpy Data

Several correlations have been developed to provide enthalpy data using computer calculations<sup>3,6,17,18</sup>. The Chao-Seader<sup>3</sup> correlation provides enthalpy data that are thermodynamically consistent with the equilibrium data calculated by the correlation. This is due to the fact that the departures from ideal enthalpies are determined using parameters obtained in the calculation of the vaporization constants.

The Chao-Seader correlation does not cover many of the systems commonly separated by extractive or azeotropic distillation. In these systems vapor-phase ideality is assumed, but partial molar heats of solution have to be calculated for the liquid phase. These partial molar heats of solution are calculated by the Redlich-Kister equation<sup>19</sup> knowing the liquid phase composition and the infinite heats of dilution. The latter are listed in the Critical Tables<sup>20</sup> for many common systems or can be obtained by a combination of the Pierotti<sup>21</sup> correlation and the relationship of the activity coefficients to the infinite heats of dilution<sup>19</sup>. Ideal enthalpies can be obtained on most hydrocarbon systems from the literature<sup>20,22</sup>.





### 2.3 Rigorous Distillation Calculations

The development of high-speed digital computers has made the rigorous solution of a distillation column possible. The most common computational techniques for the solution and design of distillation columns are variations of the methods of Thiele and Geddes and Amundson<sup>23</sup>. Both of these methods rely on the iterative technique and are extensively covered by Holland<sup>24</sup> and Smith<sup>19</sup> respectively.

Lyster<sup>25</sup> has made an extensive study of the method of Thiele and Geddes as applied to simple and complex distillation columns. The model developed by Amundson<sup>23</sup> was the first attempt at setting the column material and enthalpy balance equations in a matrix form. Amundson<sup>23</sup> solved the matrix by inversion, however, which introduced instabilities.

The simultaneous solution of the column matrix using a modified Gauss elimination technique was lately proposed by Wang and Henke<sup>26</sup>. This method of solution is claimed<sup>26</sup> to be numerically more stable and more accurate than the inversion method since it totally avoids the subtraction of nearly equal quantities. The Muller method<sup>27</sup>, which is claimed to cut solution times by at least a factor of three over the Erbar technique<sup>28</sup>, was used in this work to determine the bubble-point stage temperatures. The method is studied and recommended by Lapidus<sup>29</sup>.



## 2.4 Rigorous Design of Extractive Distillation

Relatively few studies have been reported on the rigorous design of extractive distillation. The topic is dealt with by Smith<sup>19</sup> who presents the first iteration in the design of an extractive distillation column for the separation of methylcyclohexane and toluene. Coates<sup>30</sup> describes the phenomena that take place inside an extractive distillation column and lists the general properties that a solvent must possess. The choice of the solvent can be made using the molecular similarity technique<sup>31</sup> where the solvent is chosen according to the hydrogen-bond capability that both the system and the solvent possess, or by use of the Pierotti<sup>21</sup> correlation. Dunn<sup>32</sup> et al provide classical data as to the effect of solvent concentration on the vapor-liquid equilibria of a system to be separated. They also describe the result of their work on the optimization of an extractive distillation column. As for the simulation of multicomponent distillation columns, a research in the literature could not locate any work dealing with that topic.





### III. FUNDAMENTAL CONSIDERATIONS IN EXTRACTIVE DISTILLATION

#### 3.1 General

Whenever the components in a system to be fractionated boil too closely together to be economically separated by simple distillation, azeotropic or extractive distillation may be resorted to. In both these cases a third component, called "entrainer" or "solvent" respectively is added to the system. This addition causes a modification of the deviations from Raoult's law that each component exhibits<sup>19</sup>.

This modification is obtained by:

- a) The choice of the third component
- b) The concentration of the third component in the system.

In the case of azeotropic distillation the "entrainer" forms an azeotrope with one or both of the components in the system. This facilitates the separation since most binary azeotropes are lower boiling than any of the pure components that constitute the azeotrope. In extractive distillation, the "solvent" ideally enhances the volatility of the naturally more volatile component in the system. The solvent itself boils so far above any of the pure-feed components that the possibility of forming azeotropes is usually quite remote. This also causes it to always leave a distillation column at the bottom.



### 3.2 Desirable Solvent Properties

Coates<sup>30</sup> lists the general properties that a solvent must possess for the successful extractive distillation of a system. These are:

- 1) The solvent should be non-corrosive, readily available, non-reactive with the components to be separated, and of much lower volatility with respect to them.
- 2) It should cause a greater increase in the volatility of one component than in that of the other.
- 3) The solvent should avoid the formation of immiscible liquid phases and/or azeotropes with either of the components to be separated.

### 3.3 Selection of the Solvent

One general approach in the selection of a solvent is to find a compound that is chemically similar to the high boiling key. A high-boiling homolog to this compound is then used as the separating agent to avoid azeotropic formation between the chemically-similar compounds.

The fact that the solvent is similar to the higher boiling key causes it to behave more ideally with that key than with the light key. This causes the light key to exhibit greater positive deviations from Raoult's law.





Table 3.1 illustrates this method for acetone and methanol with respective boiling points of 56.4 and 64.7°C<sup>19</sup>. If acetone is the heavy key in a mixture to be separated, then any of its four listed homologs could be used as a solvent provided it does not form an azeotrope with the light-key. If acetone is the light key, such as in an acetone-methanol mixture, water would probably be the most suitable solvent due to its ready availability and its easy handling characteristics. According to this method, then, the lowest-boiling homolog of the heavy key that does not form an azeotrope with the light key is the most suitable solvent.

Table 3.1

Homologs of Acetone and Methanol Respectively

<u>Solvent</u>	<u>B.P. °C</u>	<u>Solvent</u>	<u>B.P. °C</u>
Methyl Ethyl Ketone	79.6	Ethanol	78.3
Methyl n-Propyl Ketone	102.0	Propanol	97.2
Methyl i-Butyl Ketone	115.9	Water	100.0
Methyl n-Amyl Ketone	150.6	Butanol	117.8
		Amyl Alcohol	137.8
		Ethylene Glycol	197.2





If the concept of molecular similarity is insufficient in the choice of a solvent, two semi-quantitative methods are available. Ewell et al<sup>31</sup> divided all liquids, depending on their hydrogen-bond forming capabilities, into five classes. Since any reduction of the intermolecular bonds in a system will lead to more mobility and a higher volatility of its components, the direction and approximate extent of the deviation from Raoult's law caused by mixing any two of the classes of liquids could be predicted from the classification. However, the hydrogen bond is only one of the intermolecular forces that could exist in a system. Consequently, this classification fails to predict, for example, the increased volatility in aromatic hydrocarbons when a paraffin is added, even though both fall in the class of liquids having no hydrogen bond-forming capabilities<sup>19</sup>.

Pierotti et al<sup>21</sup> offer a method for predicting deviations from Raoult's law more quantitatively than is possible with Ewell's classification. The method relates the change in the excess partial molar free energy of a solute at an infinite dilution in a solvent to a series of interaction constants. Since excess partial molar free energies are directly relatable to activity coefficients, it becomes possible, through Pierotti's correlation, to predict the influence of the molecular structure of solvent or solute on the volatilities of the components in a system.



### 3.4 Solvent Concentration

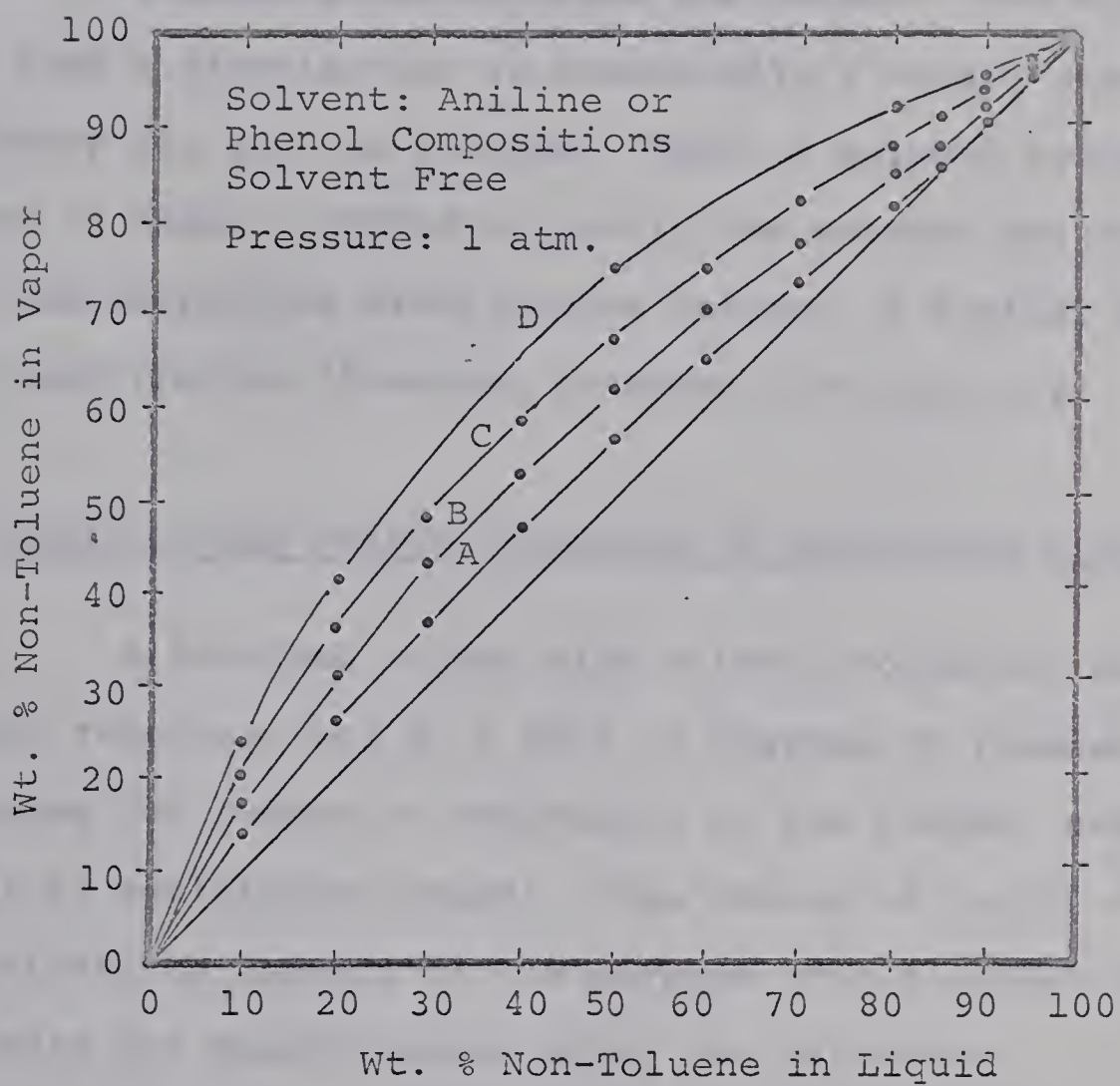
An extension of both the molecular similarity concept and the hydrogen-bond concept would be that increasing the solvent concentration in a liquid mixture could enhance the volatility of the solute. This is found experimentally to be true. Classical data in this respect are those of Souders et al<sup>32</sup>. Figure 3.1 shows the effect of varying the solvent concentration on the ratio of non-toluene to toluene in the vapor-phase of such mixtures (on a solvent-free basis). The non-toluene mixture is a narrow cut from a straight-run naphtha. These data show that as the concentration of the extractive agent increases, the column required for a given separation will be shorter when all other specifications are kept constant. On the other hand, the increase in the solvent will require increased heat loads and column diameters, so that an economic balance can be struck between the advantages and disadvantages of increased solvent concentration.

### 3.5 Description of an Extractive Distillation Column

A typical extractive distillation column will consist of three sections. The function of each section can be thought of as follows<sup>30</sup>: the section between the top of the column and the solvent introduction point is the "solvent recovery section". It removes the solvent from the







- A No Solvent
- B 25% wt. Solvent in Liquid
- C 50% wt. Solvent in Liquid
- D 75% wt. Solvent in Liquid

Figure 3.1 Vapor-Liquid Equilibrium for Mixtures of Toluene-Non-Toluene





vapors going up the column. The section between the solvent and the feed introduction points removes from the vapor phase the heavier components and is known as the "absorbing section". The "stripping section", which is below the feed, removes the light component from the liquid. The bottom product from a distillation is essentially a binary containing the heavy key and the solvent. Thus, a solvent recovery column is usually needed to purify the solvent for recycle into the extractive distillation column. A typical extractive distillation flowsheet is shown in Figure 3.2

### 3.6 Study of the Design Variables in Extractive Distillation

A two-feed column with a total condenser and a partial reboiler, has  $2C + 2N + 12$  degrees of freedom<sup>19</sup>, where C denotes the number of components in the system, and N the number of equilibrium stages. The choice of the  $2C + 2N + 12$  specifications depends on the purpose of the study, the items available for specification being the following:

Pressure in N stages	N		
Pressure in condenser			1
Pressure and heat leak in reflux divider			2
Heat leak in N-1 stages	N -		1
Reflux temperature or condenser load			1
Total number of stages			1
Fresh feed composition, temperature and rate	C	+	2
Solvent feed composition, temperature and rate	C	+	2



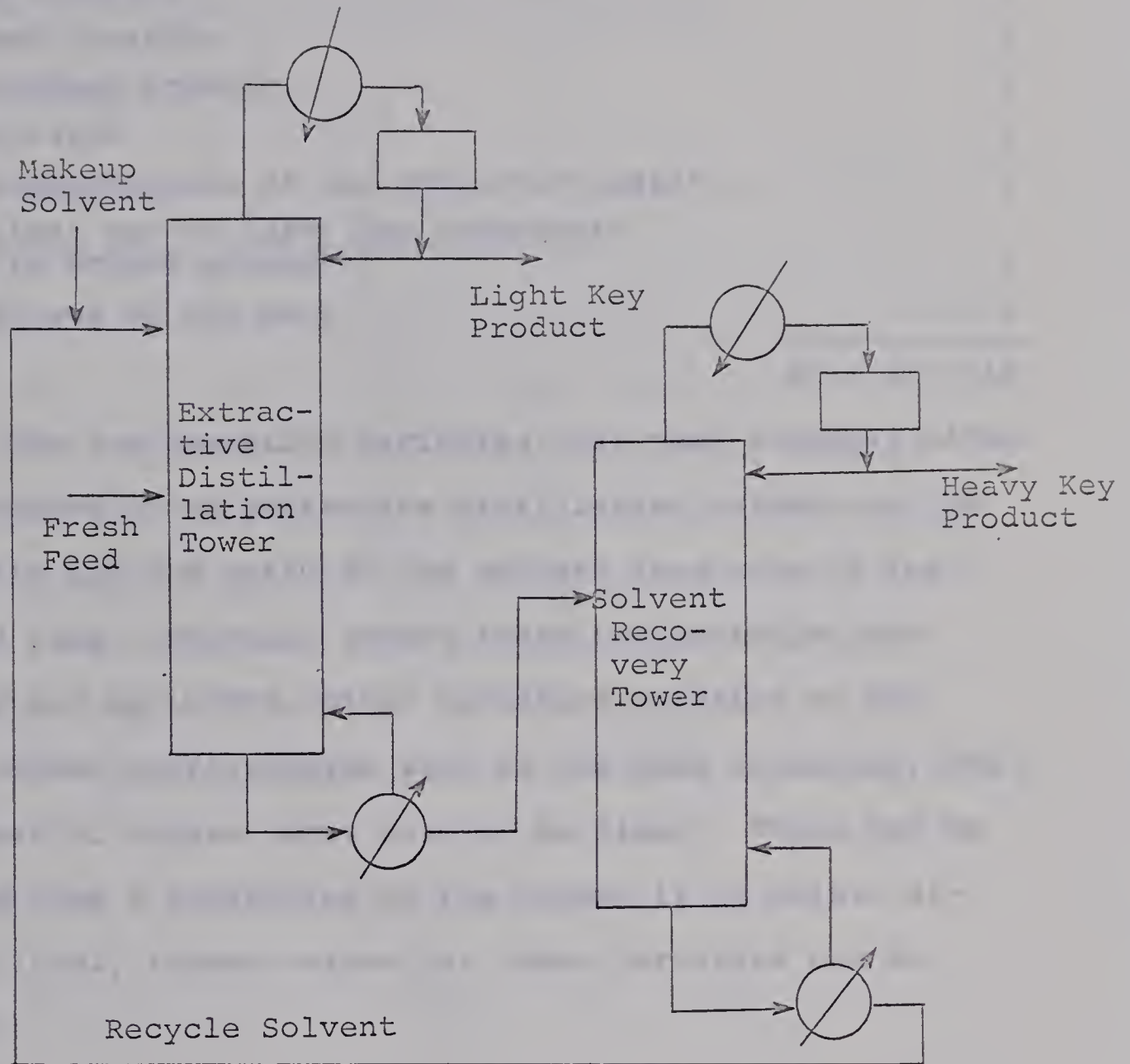


Figure 3.2 Simplified Flow Diagram for an Extractive Distillation Process





Fresh feed location	1
Solvent feed location	1
Rate of overhead product	1
One reflux ratio	1
Overhead concentration of the extractive agent	1
Ratio of light key to heavy key components in bottom product	1
Recovery of one of the keys	1
	<hr/>
	$2C + 2N + 15$

The two operating variables that most strongly affect the performance of an extractive distillation column are the reflux ratio and the ratio of the solvent feed rate to the fresh feed rate. However, before these two variables can be studied and optimized, other variables relating to the physical column configuration such as the feed locations, the total number of stages, etc. have to be fixed. These can be determined from a simulation of the column if it exists already, or likely random values for these variables can be specified.



#### IV. GENERALIZED MODEL FOR DISTILLATION

##### 4.1 The Pertinent Equations

The purpose of any rigorous calculation method in distillation design is the determination of the unique set of flow rates, temperatures and compositions that will exist in the column. To obtain such a unique solution a necessary and sufficient number of variables has to be specified in advance. The basic concept used in all distillation models is the equilibrium stage shown in Figure 4.1 where the vapor and liquid streams leaving the stage are assumed to be in equilibrium.

The equations relating to this model can be expressed as follows:

- 1) The component i material balance around stage j

$$\begin{aligned} L_{j-1}x_{i,j-1} - (V_j + W_j)y_{ij} - (L_j + U_j)x_{ij} \\ + V_{j+1}y_{i,j+1} + F_jz_{ij} = 0 \end{aligned} \quad (4.1)$$

- 2) The equilibrium relationship

$$y_{ij} - K_{ij}x_{ij} = 0 \quad (4.2)$$

- 3) The restriction on fractional concentrations

$$\sum x_{ij} = 1.0 \quad \text{and} \quad \sum y_{ij} = 1.0 \quad (4.3)$$



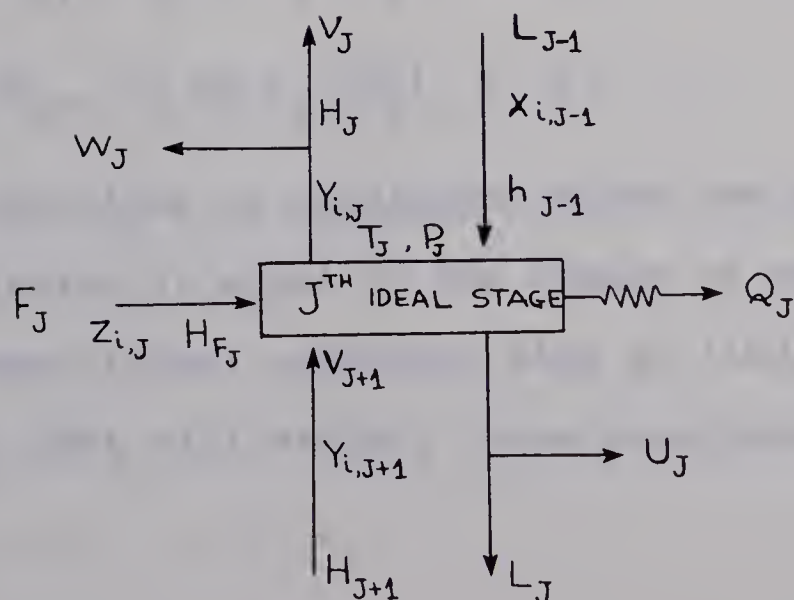
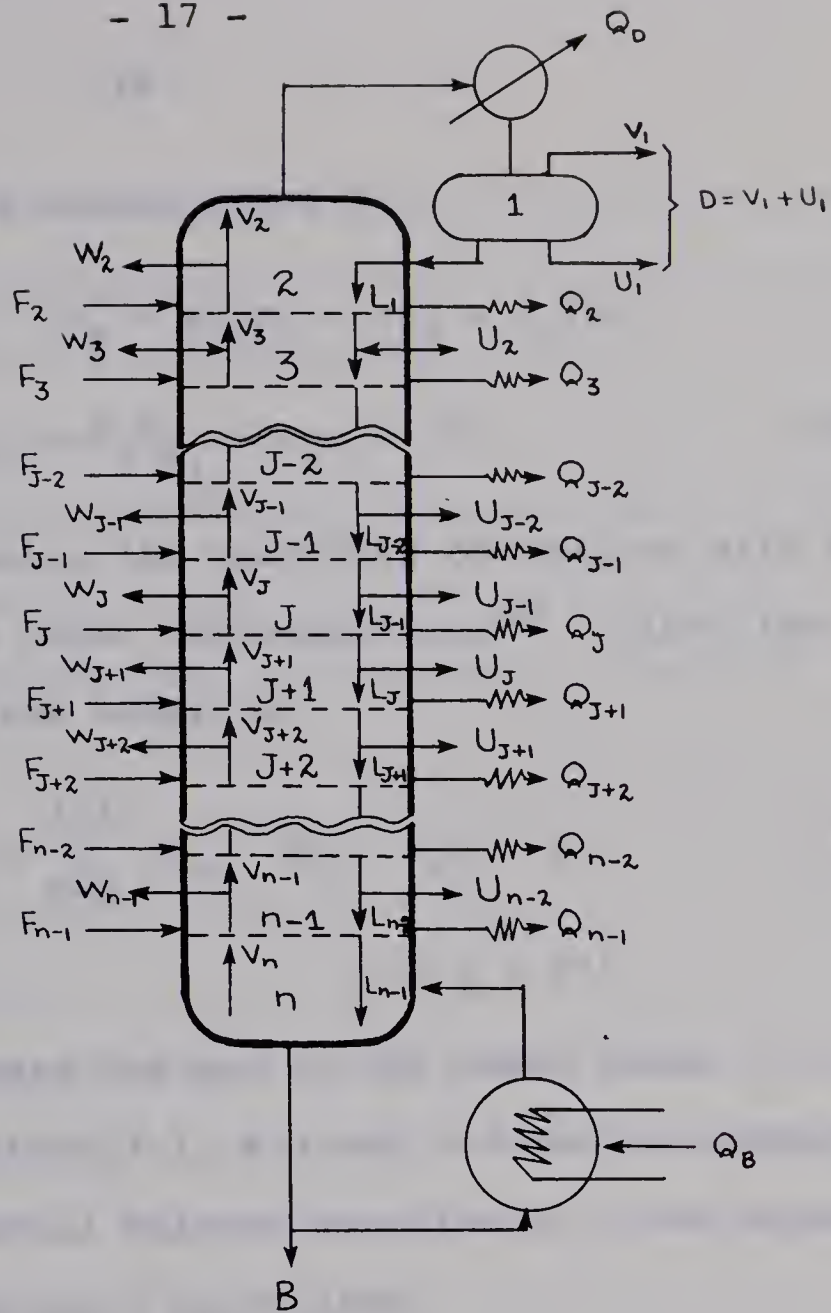


Figure 4.1 The Model Column and the Equilibrium Stage





4) The energy balance around atage j

$$\begin{aligned} L_{j-1}h_{j-1} - (V_j + W_j)H_j - (L_j + U_j)h_j \\ + V_{j+1}H_{j+1} + F_jH_{F_j} - Q_j = 0 \end{aligned} \quad (4.4)$$

Equation (4.2) eliminates the necessity of dealing with vapor concentrations in the other three equations<sup>36</sup>. Also, the overall material balance equation

$$L_{j-1} = V_j + \sum_{k=2}^{j-1} (F_k - W_k - U_k) - D \quad (4.5)$$

$$2 \leq j \leq n-1$$

can be used to eliminate one set of the phase rates  $V_j$  or  $L_j$ . Thus, the above equations 4.1, 4.3 and 4.4 can be respectively represented as a material balance equation M, a sum equation S, and an energy equation E as follows.

$$M_{ij}(x_{ij}, V_j \text{ or } L_j, T_j) = 0 \quad (4.6)$$

$$S_j(x_{ij}, V_j \text{ or } L_j, T_j) = 0 \quad (4.7)$$

$$E_{ij}(x_{ij}, V_j \text{ or } L_j, T_j) = 0 \quad (4.8)$$

This system of equations is consistent since the number of independent variables is equal to the number of equations. Any rigorous computational procedure aims at finding the set of  $x_{ij}, V_j$  and  $T_j$  that will satisfy these equations.



The M-equation provides a liquid composition vector when the  $V_j$  and  $T_j$  profiles are available. A detailed presentation of the methods available for the solution of this equation is given by Smith<sup>19</sup>. More recently, Wang and Henke<sup>26</sup> proposed an algorithm for the solution of the M-matrix that does not involve the subtraction of nearly equal numbers. Thus, it preserves accuracy and is numerically stable<sup>26</sup>.

Equation (4.7) is solved for the temperature vector in the column. The solution of this equation involves a trial and error procedure to find the temperature at every stage that satisfies one of the conditions of equation (4.3) (dew point or bubble point temperatures respectively). The E-equation is the energy balance equation which provides the flow rates in the column. Except for the case of high-boiling components, direct algebraic solution of equation (4.8) is found to be quite adequate.

The approach used in this work to solve equations (4.6) to (4.8) is outlined in the following sections.

#### 4.2 Solution of the Material Balance Equations

Figure 4.1 also represents the model column used to derive the working equations.

The column has  $N$  equilibrium stages. A partial or total condenser is the first stage, and the reboiler is the  $N^{\text{th}}$  stage. The model is derived for the most complex





conditions possible: each stage includes a feed stream,  $F_j$ , one vapor and one liquid side stream,  $W_j$  and  $U_j$  respectively, and one heat exchange device with load  $Q_j$ .

To derive the solution algorithm, we rewrite the material balance equation (4.1) after the substitution for  $y_{ij}$  from (4.2):

$$\begin{aligned} L_{j-1}x_{i,j-1} - (V_j + W_j)K_{ij}x_{ij} - (L_j + U_j)x_{ij} \\ + V_{j+1}K_{i,j+1}x_{i,j+1} + F_jZ_{ij} = 0 \end{aligned} \quad (4.9)$$

Collecting terms

$$\begin{aligned} L_{j-1}x_{i,j-1} - \left[ (V_j + W_j)K_{ij} + (L_j + U_j) \right] x_{ij} \\ + V_{j+1}K_{i,j+1}x_{i,j+1} = -F_jZ_{ij} \end{aligned} \quad (4.10)$$

Defining

$$B_j = - \left[ (V_j + W_j)K_{ij} + (L_j + U_j) \right] \quad 2 \leq j \leq n-1 \quad (4.11)$$

$$C_j = V_{j+1}K_{i,j+1} \quad 2 \leq j \leq n-1 \quad (4.12)$$

$$\begin{aligned} A_j &= L_{j-1} \\ &= V_j + \sum_{k=2}^{j-1} (F_k - W_k - U_k) - D \end{aligned} \quad 2 \leq j \leq n-1 \quad (4.5)$$

$$D_j = -F_jZ_{ij} \quad 2 \leq j \leq n-1 \quad (4.13)$$



and substituting into equation (4.10)

$$A_j x_{i,j-1} + B_j x_{ij} + C_j x_{i,j+1} = D_j$$

$$2 \leq j \leq n-1 \quad (4.14)$$

This equation now lends itself to matrix notation as follows:

$$\begin{bmatrix} B_1 & C_1 & & & \\ A_2 & B_2 & C_2 & & \\ & A_j & B_j & C_j & \\ & & A_{n-1} & B_{n-1} & C_{n-1} \\ & & & A_n & B_n \end{bmatrix} \begin{bmatrix} x_{i1} \\ x_{i2} \\ x_{ij} \\ x_{i,n-1} \\ x_{in} \end{bmatrix} = \begin{bmatrix} D_1 \\ D_2 \\ D_j \\ D_{n-1} \\ D_n \end{bmatrix} \quad (4.15)$$

Thus, the material balance equations in the column reduce to a tridiagonal matrix notation. One algorithm to solve for  $\{x\}$  is offered by Wang and Henke<sup>26</sup>, derived from a Gauss elimination method. In this method of solution, two auxiliary quantities  $p_j$  and  $q_j$  are first calculated across the column:

$$p_1 = \frac{C_1}{B_1} ; \quad q_1 = \frac{D_1}{B_1} \quad (4.16)$$

$$p_j = \frac{C_j}{B_j - A_j p_{j-1}} \quad 2 \leq j \leq n-1 \quad (4.17)$$

$$q_j = \frac{D_j - A_j q_{j-1}}{B_j - A_j p_{j-1}} \quad 2 \leq j \leq n \quad (4.18)$$



With the vectors  $\{p_j\}$  and  $\{q_j\}$  available, the liquid composition at the bottom stage is calculated first. then  $j$  is decreased till  $x_{i1}$  is reached. Thus,

$$x_{iN} = q_N \quad (4.19)$$

$$x_{ij} = q_j - p_j x_{i,j+1} \quad 1 \leq j \leq n-1 \quad (4.20)$$

This algorithm provides a simple method for the solution of the matrix equation (4.15).

#### 4.3 Determination of the Temperature Profile

When the composition of a liquid and the equilibrium constants of its components are available, the problem is to find a value of  $T_j$  such that the second condition in equation (4.3) is satisfied. Several approaches are used in the determination of this bubble-point temperature.

One approach is to use Newton's method. Rearranging equation (4.3) in functional notation gives

$$f(T) = \sum_{i=1}^C K_i x_i - 1.0 \quad (4.21)$$

Thus, the positive value of  $T$  is to be found such that  $f(T) = 0$ . Since each of the  $K_i$ 's increases with temperature,  $f(T)$  has only one root.

If  $T_n$  is the assumed value of  $T$  for trial number  $n$ , the temperature used in the next iteration,  $T_{n+1}$ , is given





by Newton's formula

$$T_{n+1} = T_n - \frac{f(T_n)}{f'(T_n)} \quad (4.22)$$

where

$$f'(T) = \sum_{i=1}^C x_i \left( \frac{dK_i}{dT} \right) \quad (4.23)$$

= the first derivative of  $f(T)$

Thus, Newton's method consists in drawing successive tangents to the  $f(T)$  vs.  $T$  curve. Convergence with this method is not guaranteed. Depending on the initial guess of  $T$  and the particular shape of  $f(T)$ , convergence may or may not occur. If  $f(T)$  has turning points or inflections in the interval of interest,  $T_{n+1}$  may be further away from the desired root than  $T_n$ <sup>37</sup>.

Another disadvantage of this method is the need to determine  $(dK_i/dT)$  which is almost impossible if  $K_i$  is a complex function of temperature, pressure, and composition such as in Chao-Seader<sup>3</sup> or Prausnitz<sup>4</sup> models.

Another approach for the determination of bubble-point temperatures is the regula-falsi method. Here, two arbitrary values of  $T$  are selected. Denoting these by  $T_n$  and  $T_{n+1}$ , the next best value  $T_{n+2}$  can be obtained from

$$T_{n+2} = \frac{T_n f(T_{n+1}) - T_{n+1} f(T_n)}{f(T_{n+1}) - f(T_n)} \quad (4.24)$$



This technique, however, is inefficient and again convergence is not guaranteed.

Wang and Henke<sup>26</sup> report good success in bubble-point temperature determinations using Muller's method<sup>27</sup>. This is the method that has been used in this work exclusively. Muller's method consists in making three arbitrary estimates of the root desired ( $\bar{T}$ )<sup>29</sup>. The next estimate is based upon fitting a second-degree Lagrangian interpolation formula to the points  $\left[ f(T^{(0)}), T^{(0)} \right]$ ,  $\left[ f(T^{(1)}), T^{(1)} \right]$ , and  $\left[ f(T^{(2)}), T^{(2)} \right]$  and finding  $T^{(3)}$ , where  $T^{(0)}$ ,  $T^{(1)}$ , and  $T^{(2)}$  are the estimated roots. The next iteration then uses  $T^{(3)}$ ,  $T^{(1)}$  and  $T^{(2)}$  as the estimates and  $T^{(4)}$  becomes the new root, etc. The iteration process is continued until  $|T^{(n)} - T^{(n-1)}| \leq \epsilon$  where  $\epsilon$  is a predetermined tolerance in the value of the root.

The equation determining the choice of the next root is

$$T_k = T_{k-1} + (T_{k-1} - T_{k-2}) * d_k \quad k \geq 4 \quad (4.25)$$

where

$$d_k = \frac{-2 * f(T_{k-1}) * (1 + d_{k-1})}{b \pm \sqrt{b^2 - 4 * f(T_{k-1}) * d_{k-1} * (1 + d_{k-1}) * C}} \quad (4.26)$$

$k \geq 4$

In equation (4.26)

$$C = f(T_{k-3}) * d_{k-1} - f(T_{k-2}) * (1 + d_{k-1}) + f(T_{k-1}) \quad (4.27)$$





and

$$b = f(T_{k-3}) * (d_{k-1})^2 - f(T_{k-2}) * (1 + d_{k-1})^2 + f(T_{k-1}) * (1 + 2*d_{k-1}) \quad (4.28)$$

Equation (4.26) will yield two roots due to the  $\pm$  notation in the denominator. If one of these roots is negative it is immediately rejected. If both roots are positive, the root that yields a value of  $\sum_{i=1}^N y_i$  closer to 1.0 is accepted.

Equation (4.25) is iterated upon until the temperature that satisfies equation (4.3) is determined. No lack of convergence has been experienced with this method. Of importance in this method is that the starting values for the iteration are not special and  $f'(T)$  need not be evaluated<sup>29</sup>. The method is graphically presented in Figure 4.2

#### 4.4 Solution of the Energy Balance Equations

The conventional method of the solution of the energy balance equations has been exclusively followed in this work. An energy balance around the equilibrium stage shown in Figure 4.1 can be written as follows:

$$L_{j-1}h_{j-1} - (V_j + W_j)H_j - (L_j + U_j)h_j + V_{j+1}H_{j+1} + F_jH_{F_j} - Q_j = 0 \quad (4.4)$$



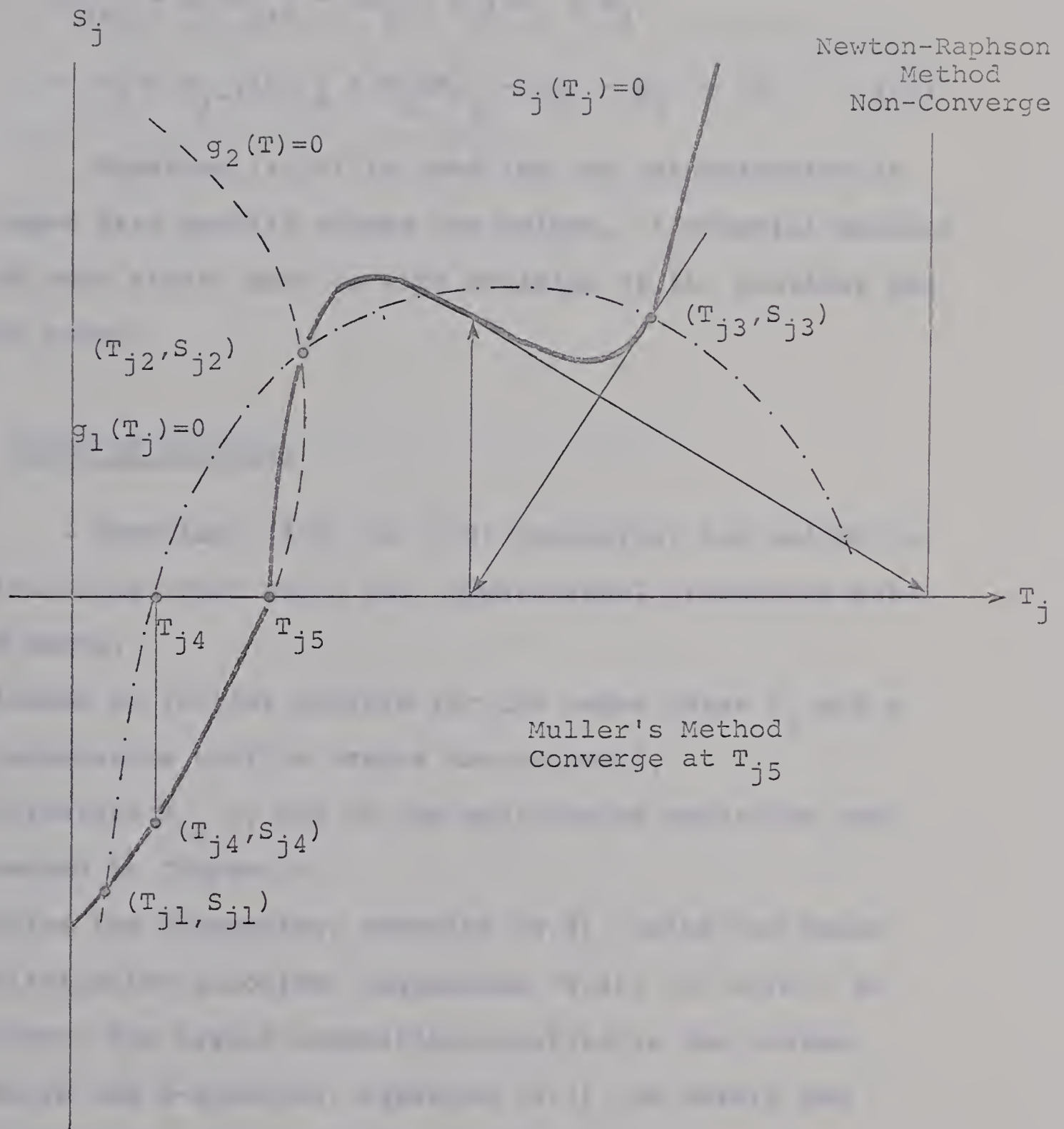


Figure 4.2 Graphical Comparison of Muller's Method to Newton-Raphson



rearranging terms and substituting for  $L_j$  from a material balance

$$\begin{aligned} & (H_{j+1} - h_j)V_{j+1} - (H_j - h_j)(V_j + W_j) \\ & - (h_j - h_{j-1})L_{j-1} + F_j(H_{F_j} - h_j) - Q_j = 0 \end{aligned} \quad (4.29)$$

Equation (4.29) is used for the determination of the vapor rate profile across the column. A material balance around each stage, such as with equation (4.5), provides the liquid rates.

#### 4.5 Order of Solution

Equations (4.6) to (4.8) inclusive, are solved in the following order using the computational procedures outlined above:

- 1) Assume an initial profile for the vapor phase  $V_j$  and a temperature profile across the column  $T_j$ .
- 2) Calculate  $K_{ij}$  by any of the equilibrium equations presented in Chapter V.
- 3) Solve the M-equation, equation (4.6), using the Gauss elimination algorithm (equations (4.16) to (4.20)) to obtain the liquid composition profile in the column.
- 4) Solve the S-equation, equation (4.7), to obtain the temperature vector in the column.
- 5) Calculate the enthalpies of the streams by one of the methods presented in Chapter V.





- 6) Solve the E-equation for a new set of  $V_j$ .
- 7) Repeat steps 2 to 6 until the sum of the squares of the stage temperatures between any two successive iterations is less than a certain value, usually  $0.01 N$ , where  $N$  is the number of stages.



## V. CALCULATION OF EQUILIBRIUM AND ENTHALPY DATA

The solution of the material balance equations in a column requires equilibrium data for the components being distilled. Enthalpy data on the phases in equilibrium are necessary for the energy balance equations. The methods that are in use to obtain such data will be discussed in this chapter.

### 5.1 Polynomial Presentation of K and H Data

In order to render the large quantity of experimental equilibrium and enthalpy data available to a computer, it is necessary to represent the data in equation form. Several curve-fitting techniques have been tried for this purpose, with polynomial presentation being most suitable due to its ease of handling. Examples of this form of data presentation is the polynomial presentation of the equilibrium ratios of twelve hydrocarbon components originally presented graphically in the NGAA data book <sup>5</sup>. These charts correlated K-ratios in terms of temperature and pressure, the effect of composition being taken into account by the additional parameter known as the convergence pressure.

Another example of this form of data presentation is the Yen and Alexander<sup>17</sup> enthalpy correlation, whereby





enthalpy departures of some hydrocarbon components can be calculated from a polynomial curve-fit of Rossini's<sup>6</sup> data using Forsythe polynomials.

Although with increasing sophistication in curve-fitting techniques, data presentation by this method might gain wider applications, some disadvantages are inherent in them, the most serious being the discreteness of the conditions for which data can be retrieved. For example, K-ratios can only be obtained at definite convergence pressures, and H-data only within defined limits of reduced properties. As a result of this inability to "predict" data, new information is needed every time a problem is run at new conditions.

## 5.2 The Chao-Seader Correlation for Equilibrium Ratios

The correlation offered by Chao and Seader<sup>3</sup> for the calculation of K ratios for hydrocarbons of various molecular types is amenable to machine computation. K's are calculated by combining three factors as follows:

$$K_i = \frac{\mu_i \gamma_i}{\phi_i} \quad (5.1)$$

In this equation,  $\mu_i$  is the f/p ratio in the liquid phase

$\gamma_i$  is the activity coefficient in the liquid phase

$\phi_i$  is the fugacity coefficient in the vapor phase



$\mu_i$  is calculated by combining a term for the fugacity coefficient of a simple fluid with a correction factor for real fluids as follows:

$$\log \mu_i = \log \mu_i^O + \omega \log \mu_i^1 \quad (5.2)$$

where

$$\begin{aligned} \log \mu_i^O = & A_O + \frac{A_1}{T_r} + A_2 T_r + A_3 T_r^2 + A_4 T_r^3 \\ & + (A_5 + A_6 T_r + A_7 T_r^2) P_r + (A_8 \\ & + A_9 T_r^2) P_r^2 - \log P_r \end{aligned} \quad (5.3)$$

and

$$\begin{aligned} \log \mu_i^1 = & 4.23893 - 8.65808 T_r - \frac{1.22060}{T_r^3} \\ & - 3.15224 T_r - 0.025 (P_r - 0.6) \end{aligned} \quad (5.4)$$

The constants used in equation (5.3) are specific for methane, nitrogen, hydrogen, carbon dioxide and hydrogen sulfide and common for all other components handled by this correlation. Oxygen and carbon monoxide use the same constants as methane. These constants were tabulated by Erbar<sup>7</sup>. (Appendix III)

$\gamma_i$  is calculated from the following equation:

$$\ln \gamma_i = \frac{V_i^L (\partial_i - \partial_m)^2}{RT} \quad (5.5)$$

where

$$\partial_m = \frac{\sum_{i=1}^{NCP} \partial_i X_i V_i^L}{\sum_{i=1}^{NCP} X_i V_i^L} \quad (5.6)$$



This is the Scatchard-Hildebrand model and assumes hydrocarbon solutions to be regular i.e. to have no excess entropy of mixing.

The determination of  $\phi_i$  uses the Redlich-Kwong equation of state in the form

$$\ln \phi_i = (Z-1) \frac{B_i}{B_m} - \ln(Z - B_m P) - \frac{A_m^2}{B_m} \left( \frac{2A_i}{A_m} - \frac{B_i}{B_m} \right) * \ln(1+h) \quad (5.7)$$

where

$$Z = \frac{1}{1-h} + \frac{A_m^2}{B_m} \left( \frac{h}{1+h} \right) \quad (5.8)$$

$$h = \frac{B_m P}{Z} \quad (5.9)$$

$$A_m = \sum y_i A_i \quad (5.10)$$

$$B_m = \sum y_i B_i \quad (5.11)$$

$$A_i = \left( \frac{0.4278}{P_c T_r^{2.5}} \right)^{0.5} \quad (5.12)$$

and

$$B_i = \frac{0.0867}{P_r T_r} \quad (5.13)$$

Since (5.8) is implicit in Z it is solved by trial-and-error.





### 5.3 Chao-Seader Correlation for Enthalpy Calculations

Edmister et al<sup>18</sup> have extended the Chao-Seader correlation to the calculation of vapor and liquid enthalpies in hydrocarbon mixtures.

The vapor phase enthalpies are calculated from

$$H_m = \sum y_i H_i^o + \frac{3}{2} \frac{A_m^2}{B} \ln \left( 1 + \frac{B_m P}{Z} \right) + 1 - Z \quad (5.14)$$

The first term represents the enthalpy of a gas mixture at the ideal gas state pressure of zero. The second term represents deviations from ideality due to pressure.

Liquid phase enthalpies are calculated from the relationships

$$h_m = \sum h_i \quad (5.15)$$

where

$$h_i = H_i^o - RT_r^2 T_c \left| \left( \frac{\partial \ln \mu_i}{\partial T_r} \right)_P + \left( \frac{\partial \ln \gamma_i}{\partial T_r} \right)_{P, x_i} \right| \quad (5.16)$$

$$\begin{aligned} \left( \frac{\partial \ln \mu_i}{\partial T_r} \right)_P = 2.303 \left| - \frac{A_1}{T_r^2} + A_2 + Z A_3 T_r^2 + 3 A_4 T_r \right. \\ \left. + (A_6 + 2 A_7 T_r) P_r + A_9 P_r^2 + \omega_i (A_{11} \right. \\ \left. - \frac{A_{12}}{T_r^2} + 3 A_{13} T_r^2) \right| \quad (5.17) \end{aligned}$$



and

$$\left(\frac{\partial \ln \gamma_i}{\partial T_r}\right)_{P, x_i} = \frac{V_i^L}{RT_r^2 T_c} (\partial_m - \partial_i)^2 \times 1.8 \quad (5.18)$$

$H_i^O$ , the ideal gas state enthalpy of a component, is calculated from a cubic equation in temperature as follows:

$$H_i^O = AH_i + (BH_i)T + (CH_i)T^2 + (DH_i)T^3 \quad (5.19)$$

where the coefficients are tabled for all the components that can be handled by the correlation.

#### 5.4 The Prausnitz Equilibrium Model Based on Wilson's Equation

In 1964 Wilson<sup>14</sup> proposed a model that could calculate liquid phase activity coefficients in multicomponent systems using only parameters obtainable from the binary data. Orye and Prausnitz<sup>4</sup> described a vapor-liquid equilibrium model in which they proposed to incorporate the Wilson equation. This equilibrium model was further developed by O'Connell et al<sup>10</sup> and Lyckman et al<sup>8</sup>, and is presented in this section.

For equilibrium between a vapor and a liquid phase, the condition to be satisfied is the equality of the fugacities of the two phases, i.e.

$$f_i^L = f_i^V \quad (5.20)$$





These terms can be developed as follows<sup>10</sup> :

$$f_i^L = \gamma_i x_i f_i^{o(po)} \exp \left( \frac{P \bar{v}_i^L}{RT} \right) \quad (5.21)$$

and

$$f_i^V = \phi_i y_i P \quad (5.22)$$

Substituting in (5.20) yields the equilibrium equation presented by Orye and Prausnitz<sup>4</sup> thus:

$$\phi_i y_i P = \gamma_i x_i f_i^{o(po)} \exp \left( \frac{\bar{v}_i^L P}{RT} \right) \quad (5.23)$$

From this equation

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i f_i^{o(po)} \exp \left( \frac{\bar{v}_i^L P}{RT} \right)}{\phi_i P} \quad (5.24)$$

The meaning and computation of each term will be developed separately.

### The Fugacity Coefficient of the Vapor-Phase ( $\phi_i$ )

This term can be calculated from

$$\ln \phi_i = \frac{2}{\bar{v}} \sum_{j=1}^{NCP} y_j B_{ij} - \ln Z \quad (5.25)$$

where

$Z$  = compressibility factor

$\bar{v}$  = molar volume of the vapor mixture

$B$  = second virial coefficient of the i-j interaction



Z and B are related by

$$Z = 1 + \frac{\left( \sum_{i=1}^{NCP} \sum_{j=1}^{NCP} Y_i Y_j B_{ij} \right)}{\bar{v}} \quad (5.26)$$

The virial coefficient is calculated from Pitzer and Curl's<sup>12</sup> correlation for non-polar gases. This correlation was reported by Lewis and Randall<sup>13</sup>. For polar gases a recent publication by O'Connell and Prausnitz<sup>9</sup> offers a correlation based on an extended theory of corresponding states.

The Reference Fugacity in the Liquid Phase  $f_i^{o(po)}$

$f_i^{o(po)}$  is the fugacity of the saturated liquid component i at zero pressure. It is defined<sup>10</sup> as

$$f_i^{o(po)} = P_i^s \phi_i^s \exp \left( - \frac{\bar{v}_i^L P_i^s}{RT} \right) \quad (5.27)$$

where

$P_i^s$  is the saturation vapor pressure at T

$\phi_i^s$  is the vapor fugacity coefficient at  $P_i^s$  and T

$\bar{v}_i^L$  is the molar liquid volume at T

Lyckman<sup>23</sup> defines the quantity  $\psi$  such that

$$\psi = \frac{f_i^{o(po)}}{P_{c_i}} \quad (5.28)$$

where  $P_{c_i}$  is the critical pressure of i. A correlation is then presented where  $\psi$  is a function of the reduced temperature and the acentric factor of the component  $\omega$ . Pitzer suggests the following form for  $\psi$ :



$$\log \psi = \log (\psi)^0 + \omega \log (\psi)^1 \quad (5.29)$$

where  $\log (\psi)^0$  and  $\log (\psi)^1$  are each functions of the reduced temperature. Lyckman et al<sup>8</sup> present this functionality in table form and they have been polynomially fitted vs.  $T_r$  for purposes of this work as follows:

$$\begin{aligned} \log (\psi)^0 = & -14.8016 + 49.4529 T_r - 71.3050 T_r^2 \\ & + 54.1713 T_r^3 - 21.0864 T_r^4 \\ & + 3.3213 T_r^5 \end{aligned} \quad (5.30)$$

$$\text{variance} = +0.56048 \times 10^{-5}$$

and

$$\begin{aligned} \log (\psi)^1 = & -54.2280 + 409.1308 T_r - 1538.1941 T_r^2 \\ & + 3445.8673 T_r^3 - 4812.2940 T_r^4 \\ & + 4221.5419 T_r^5 - 2259.4562 T_r^6 \\ & + 674.3256 T_r^7 - 86.0182 T_r^8 \end{aligned} \quad (5.31)$$

$$\text{variance} = +0.16503 \times 10^{-4}$$

These variances being the minimum in all polynomial fits up to and including the 10<sup>th</sup> degree.

Lyckman<sup>8</sup> also offers a correlation for  $\phi_i^s$  where  $\phi_i^s$  is a function of  $T_r$  and  $\omega$ , and is represented by

$$\log \phi_i^s = \log (\phi_i^s)^0 + \omega \log (\phi_i^s)^1 \quad (5.32)$$

The table of values of  $(\phi_i^s)^0$  and  $(\phi_i^s)^1$  presented by Lyckman<sup>23</sup> have also been polynomially fitted against  $T_r$  and the relationships are as follows:





$$\begin{aligned}
 (\phi_i^s)^0 &= 53.15801 - 433.7522 T_r + 1463.0379 T_r^2 \\
 &\quad - 2611.1941 T_r^3 + 2601.3246 T_r^4 \\
 &\quad - 1372.3205 T_r^5 + 299.57934 T_r^5 \quad (5.33)
 \end{aligned}$$

$$\text{variance} = +0.6874 \times 10^{-6}$$

and

$$\begin{aligned}
 (\phi_i^s)^1 &= -0.16186 + 2.98895 T_r - 14.05742 T_r^2 \\
 &\quad + 27.77032 T_r^3 - 24.06024 T_r^4 \\
 &\quad + 7.48698 T_r^5 \quad (5.34)
 \end{aligned}$$

$$\text{variance} = 0.6299 \times 10^{-6}$$

Combining equations (5.23) and (5.27), and assuming the equality

$$\bar{v}_i^L = v_i^L \quad (5.35)$$

we obtain

$$\phi_i y_i^P = \gamma_i x_i P_i^s \phi_i^s \exp \frac{v_i^L}{RT} (P - P_i^s) \quad (5.36)$$

#### Liquid Phase Activity Coefficient $\gamma_i$

Wilson<sup>14</sup> presented a model where the excess free energy of mixing is a logarithmic series in the liquid composition and in parameters obtainable from the binary equilibria only. Orye and Prausnitz<sup>4</sup> derive the model through the following steps:



At constant temperature and pressure, an exact relationship exists between  $g^E$ , the excess Gibbs energy of mixing and  $\gamma_k$ , the activity coefficient for any component  $k$  in a liquid mixture. This relationship is

$$RT \ln \gamma_k = \left( \frac{\partial n_T^* g^E}{\partial n_k} \right)_{T,P, \text{all } n_i (i \neq k)} \quad (5.37)$$

where  $n_i$  = number of moles of component  $i$

$n_T$  = total number of moles

From the concept of athermal solutions developed by Flory<sup>15</sup> and Huggins<sup>16</sup>,  $g^E$  can be expressed as follows:

$$\frac{g^E}{RT} = \sum_{i=1}^{NCP} x_i \ln \frac{\phi_i}{x_i} \quad (5.38)$$

where

$$\phi_i = \frac{x_i v_i^L}{\sum_{i=1}^{NCP} x_i v_i^L} = \text{volume fraction of } i \quad (5.39)$$

and

$$v_i^L = \text{molar liquid volume of } i$$

From basic statistical concepts, in a binary solution of components 1 and 2, the probability of finding a type 2 molecule around a central molecule of type 1 as compared to that of finding another type 1 molecule is

$$\frac{x_{12}}{x_{11}} = \frac{x_2 \exp - \left( \frac{\lambda_{21}}{RT} \right)}{x_1 \exp - \left( \frac{\lambda_{11}}{RT} \right)} \quad (5.40)$$





where  $\lambda_{12}$  and  $\lambda_{11}$  are proportional to the 1-2 and 1-1 interaction energies

and the exponential terms are Boltzmann factors.

With this concept in mind, the volume fractions in the Flory-Huggins equation are redefined into what Wilson<sup>14</sup> terms local volume fractions

$$\xi_1 = \frac{x_1 v_1^L \exp - \left(\frac{\lambda_{11}}{RT}\right)}{x_1 v_1^L \exp - \left(\frac{\lambda_{11}}{RT}\right) + x_2 v_2^L \exp - \left(\frac{\lambda_{12}}{RT}\right)} \quad (5.41)$$

and

$$\xi_2 = \frac{x_2 v_2^L \exp - \left(\frac{\lambda_{22}}{RT}\right)}{x_2 v_2^L \exp - \left(\frac{\lambda_{22}}{RT}\right) + x_1 v_1^L \exp - \left(\frac{\lambda_{21}}{RT}\right)} \quad (5.42)$$

defining

$$\Lambda_{12} = \frac{v_2^L}{v_1^L} \exp - \left(\frac{\lambda_{12} - \lambda_{11}}{RT}\right) \quad (5.43)$$

and

$$\Lambda_{21} = \frac{v_1^L}{v_2^L} \exp - \left(\frac{\lambda_{21} - \lambda_{22}}{RT}\right) \quad (5.44)$$

and substituting into (5.41) and (5.42) then

$$\xi_1 = \frac{x_1}{x_1 + x_2 \Lambda_{12}} \quad (5.45)$$

and

$$\xi_2 = \frac{x_2}{x_2 + x_1 \Lambda_{21}} \quad (5.46)$$

substituting these local volume fractions for  $\phi_i$  in equation



(5.38) ,

$$\frac{g^E}{RT} = - \sum_{i=1}^{NCP} x_i \ln \left( \sum_{j=1}^{NCP} x_j \Lambda_{ij} \right) \quad (5.47)$$

where

$$\Lambda_{ij} = \frac{v_j^L}{v_i^L} \exp - \left( \frac{\lambda_{ij} - \lambda_{ii}}{RT} \right) \quad (5.48)$$

and

$$\Lambda_{ji} = \frac{v_i^L}{v_j^L} \exp - \left( \frac{\lambda_{ji} - \lambda_{jj}}{RT} \right) \quad (5.49)$$

substituting equation (5.47) into (5.37), a general expression for the activity coefficient can be written as follows<sup>4</sup>:

$$\begin{aligned} \ln \gamma_k &= - \ln \left( \sum_{j=1}^{NCP} x_j \Lambda_{kj} \right) + 1 \\ &\quad - \sum_{i=1}^{NCP} \frac{x_i \Lambda_{ik}}{\sum_{j=1}^{NCP} x_j \Lambda_{ij}} \end{aligned} \quad (5.50)$$

Thus, the liquid activity coefficient of every component in a mixture can be obtained from the liquid composition and parameters obtainable from the respective binary equilibria. The calculation of these parameters will be discussed in the following chapter.

From the above information then, the following steps are taken to obtain vaporization constants from equation (5.24):



- 1)  $\gamma_i$ 's at any liquid composition are obtained from the Wilson equation (5.50) using the Wilson parameters.  
The following chapter discusses means of obtaining optimum Wilson parameters.
- 2)  $f_i^{o(po)}$  is obtained from equation (5.27), where:
  - a)  $P_i^S$ , the saturated vapor pressure of component i, is obtained by the use of Antoine's equation.
  - b)  $\phi_i^S$  is obtained from the correlations represented by equations (5.32) to (5.34) inclusive.
- 3) P is the total pressure of the system.
- 4)  $\phi_i$  is calculated by equation (5.25). Simplifications to that equation are presented below.

## 5.5 The Simplified Prausnitz Model for Vapor-Liquid Equilibria

Several simplifications and approximations can be made on the vapor-liquid equilibrium equation presented above without affecting its accuracy greatly. This is particularly true if the system pressure is low<sup>11</sup>.

The fully-developed equilibrium equation has been expressed as follows:

$$\phi_i y_i P = \gamma_i x_i f_i^{o(po)} \exp \left( \frac{\bar{v}_i^L P}{RT} \right) \quad (5.23)$$

or

$$\phi_i y_i P = \gamma_i x_i P_i^S \phi_i^S \exp \left[ \frac{\bar{v}_i^L}{RT} (P - P_i^S) \right] \quad (5.36)$$





# The Fugacity Coefficient of the Vapor Phase $\phi_i$

The rigorous expression for the calculation of  $\phi_i$  is equation (5.25). However, as Eckert<sup>10</sup> points out, the determination of  $\phi_i$  requires a trial-and-error procedure since it is expressed as a function of  $y$ .

Van Ness<sup>11</sup> presents an excellent treatment of constant-composition fluid behavior which will be used here to justify some of the simplifications we can bring upon  $\phi_i$ .

At constant  $T$ ,  $\phi$  is rigorously expressed as

$$\ln \phi = - \frac{1}{RT} \int_0^P \alpha dP \quad (5.51)$$

where

$$\alpha = \frac{RT}{P} - V \quad (5.52)$$

and accordingly

$$\ln \phi = \int_0^P (Z-1) \frac{dP}{P} \quad \text{at constant } T \quad (5.53)$$

where

$$Z = \frac{PV}{RT} \quad (5.54)$$

$Z$  can be written as a power series in  $P$  explicit in  $V$  as follows<sup>11</sup>:

$$Z = 1 + \frac{BP}{RT} + \frac{(C - B^2)}{(RT)^2} P^2 + \dots \quad (5.55)$$

where  $B$  and  $C$  are second and third virial coefficients respectively. Since the virial equation truncated after the



second virial coefficient is a highly reliable equation of state at low pressures<sup>11</sup>, then equation (5.55) can be written simply as

$$Z = 1 + \frac{BP}{RT} \quad (5.56)$$

Substituting (5.56) into (5.53)

$$\ln \phi = \frac{BP}{RT} \quad (5.57)$$

To show the reliability of this equation relative to other more rigorous ones, Van Ness<sup>11</sup> shows plots of the fugacity coefficient of  $\text{SO}_2$  at three different temperatures vs. pressure. From these graphs it is clear that below a pressure of approximately 6.0 atms. at  $50^\circ\text{C}$ , equation (5.57) is reliable for this system and at  $250^\circ\text{C}$ , up to 80 atmospheres can be tolerated without much loss in accuracy. Considering that the pressure of interest is normally one atmosphere in processes such as extractive distillation and that  $\text{SO}_2$  is a highly polar gas, it was decided that for our purposes, equation (5.57) would be used to compute  $\phi$ . The correlation developed by Pitzer and Curl<sup>12</sup> and reported by Lewis and Randall<sup>13</sup> expresses  $BP_c/RT_c$  as a function of  $\omega$  and  $T_r$ . The application of this correlation to the system methyl acetate-benzene-cyclohexane yielded values such that  $1.0 \geq \phi \geq 0.950$ . The general closeness of the value of  $\phi$  to 1.0 has been confirmed by O'Connell et al<sup>9</sup>. Thus, the further simplification to  $\phi = 1.00$  was made without seriously affecting the equilibrium







predictions.

The Factor  $\phi_i^S \exp((v_i^L/RT)(P - P_i^S))$

Several authors<sup>38</sup>, in calculating liquid-phase activity coefficients from equilibrium data use the following equilibrium equation:

$$y_i P = \gamma_i x_i P_i^S \quad (5.58)$$

The simplicity of this equation makes it very attractive. It was thus decided to study the ratio  $\phi_i^S \exp((v_i^L/RT)(P - P_i^S))$ , which is the factor applied to the right-hand side of the above equation (5.58) to give the right-hand side of the rigorous equilibrium equation (5.36). For the system methyl acetate-benzene-cyclohexane at one atmosphere, this ratio ranged from 0.9730 to 1.017 in all three components. It was thus concluded that for processes such as extractive distillation where the system pressure is almost always atmospheric, assigning a value of unity to both  $\phi_i$ , the fugacity coefficient of the vapor phase, and  $\phi_i^S \exp((v_i^L/RT)(P - P_i^S))$ , the correction factor in the liquid phase would lead to a negligible loss in the accuracy of equilibrium predictions.

## 5.6 Summary

Two methods of calculating equilibrium K-values using liquid-phase activity coefficients obtained from the Wilson equation are available.



The simplified method can be described in steps as follows:

- 1) The equilibrium equation is

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i P_i^s}{P} \quad (5.59)$$

- 2) The activity coefficients  $\gamma_i$  are obtained from Wilson's<sup>4</sup> parameters  $\Lambda_{ij}$  and  $\Lambda_{ji}$ . To obtain these parameters, at least one totally described equilibrium point in every binary ( $x_1, \gamma_1, \gamma_2$ ) is needed. The  $\gamma$  values in this equilibrium point should have either been obtained from equilibrium data using equation (5.58), or this equation should be used to calculate them from the equilibrium compositions.
- 3)  $P$  is the total pressure of the system and  $P_i^s$  is the vapor pressure obtained from the Antoine equation.

The rigorous method can be described in steps as follows:

- 1) The equilibrium equation is

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i P_i^s \phi_i^s \exp \frac{v_i^L}{RT} (P - P_i^s)}{P \phi_i} \quad (5.60)$$

- 2) The activity coefficients  $\gamma_i$  are obtained from Wilson's parameters  $\Lambda_{ij}$  and  $\Lambda_{ji}$ . These parameters should be obtained from equilibria points (at least one for every binary) where the activity coefficients were calculated by the rigorous method, i.e. if  $\gamma_i$  were obtained by





equation (5.58), they should be multiplied by the

factor  $\frac{\phi_i^S \exp \frac{V_i^L}{RT} (P - P_i^S)}{\phi_i}$ . These liquid activity

coefficients should then be used to calculate  $\Lambda_{ij}$  and  $\Lambda_{ji}$ . For systems at atmospheric pressure, this factor is close to unity. However, in a rigorous calculation, this correction in  $\gamma_i$  should be made.

3)  $\phi_i^S$  is obtained from (5.32) to (5.34) inclusively.

4)  $\phi_i$  is obtained from equation (5.57).

Both the rigorous and the simplified methods were used to predict the vapor compositions of the system methyl acetate-benzene-cyclohexane. The results of the study in the form of standard deviations from the equilibrium  $y_i$ 's<sup>38</sup> is shown in Table 5.1, and shows that the two methods are comparable in accuracy. This justifies the predominant use of the simplified method in the design of extractive distillation columns in this work.

Table 5.1

Comparison of the Rigorous and Simplified  
Prausnitz Methods of Equilibrium Predictions

Pressure = 1 atm.

Standard Deviation

	Rigorous Model	Simplified Model
--	-------------------	---------------------

methyl acetate	0.03769	0.04208
benzene	0.00743	0.00752
cyclohexane	0.00842	0.00770





## 5.7 Calculation of Enthalpy Data with Heats of Solution

The enthalpies of the vapor and liquid phases leaving an equilibrium stage can be calculated from

$$H_j = \sum_{i=1}^C y_{ij} \bar{H}_{ij} \quad (5.61)$$

$$h_j = \sum_{i=1}^C x_{ij} \bar{h}_{ij} \quad (5.62)$$

where  $\bar{H}_{ij}$  and  $\bar{h}_{ij}$  are vapor and liquid partial molar enthalpies of component  $i$  in the solution. Negligible error is involved in the assumption of vapor-phase ideality, i.e. that  $\bar{H}_{ij} = H_{ij}^{19}$ , and the enthalpy of the vapor phase can be calculated from pure component enthalpies.  $h_{ij}$ 's, however, can be obtained only if partial molar heats of solution  $L_i$  are available as a function of composition. The component enthalpy in solution can then be expressed as

$$\bar{h}_{ij} = h_{ij} + L_{ij} \quad (5.63)$$

For most hydrocarbons,  $h_{ij}$  and  $H_{ij}$  can be obtained from "Data Book on Hydrocarbons"<sup>22</sup>. Enthalpies for numerous other compounds are reported in the Critical Tables<sup>20</sup>.

The partial molar heats of solution  $L_i$  can be obtained with sufficient accuracy from activity coefficient data by using the equation

$$\left( \frac{d \log \gamma_i}{d \frac{1}{T}} \right) x_i = \frac{L_i}{2.3R} \quad (5.64)$$



However,  $\gamma_i$  vs.  $T$  at constant  $x$ -data are very difficult to obtain. Thus, two methods for the calculation of the partial molar heats of solution  $L_i$  can be used.

- 1) The activity coefficients of  $i$  at infinite dilution in a reference compound  $r$  ( $\gamma_i^\infty$ ) can be obtained at various temperatures by the application of Pierrotti's correlation<sup>19</sup>. Then, using equation (5.64),  $L_{ir}^\infty$ 's can be obtained. The following expression, which is derived from the Redlich-Kister equation, is then used to obtain partial molar heats of solution at any desired composition:

$$\begin{aligned}
 L_r = & \frac{1}{2}(1-x_r) \sum_i x_i (L_{ir}^\infty + L_{ri}^\infty) - \frac{1}{2} \sum_{\substack{i \neq j \\ i \neq r}} (L_{ji}^\infty + L_{ij}^\infty) x_i x_j \\
 & + \frac{1}{2} \sum_i (L_{ir}^\infty - L_{ri}^\infty) x_i \left[ 2x_r(1-x_r+x_i) - x_i \right] \\
 & - \sum_{\substack{i \neq j \\ i \neq r}} (L_{ji}^\infty - L_{ij}^\infty) x_i x_j (x_i - x_j) \quad (5.65)
 \end{aligned}$$

where  $i, j$  and  $r$  refer to components. This equation is derived by Smith<sup>19</sup> in full detail.

- 2) Equation (5.65) can be used without recourse to Pierrotti's correlation. This is done by using "The Critical Tables"<sup>20</sup>, which are a source of a large number of experimentally determined infinite dilution partial molar heats of solution.



of solution.

mentally determined infinite dilution partial molar heats Tables<sup>20</sup>, which are a source of a large number of experimental correlation. This is done by using "The Critical

Equation (5.22) can be used without recourse to Pier-



## VI. EVALUATION OF PARAMETERS FOR THE WILSON MODEL

### 6.1 The Model

One of the methods used in this work to obtain liquid phase activity coefficients is the Wilson model. It has been presented above as follows:

$$\ln \gamma_k = - \ln \left( \sum_{j=1}^{NCP} x_j \Lambda_{kj} \right) + 1 - \frac{\sum_{i=1}^{NCP} \frac{x_i \Lambda_{ik}}{\sum_{j=1}^{NCP} x_j \Lambda_{ij}}}{\sum_{j=1}^{NCP} x_j \Lambda_{ij}} \quad (5.50)$$

For a binary solution, this reduces to

$$\begin{aligned} \ln \gamma_1 = & -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} \right. \\ & \left. - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right) \end{aligned} \quad (6.1)$$

and

$$\begin{aligned} \ln \gamma_2 = & -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} \right. \\ & \left. - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right) \end{aligned} \quad (6.2)$$

It can be seen from these equations that the liquid activity coefficients of the components in a solution can be obtained as a function of the composition in the solution and the parameters  $\Lambda_{ij}$ , called Wilson's parameters, which are obtain-



able from the binary data.  $\Lambda_{ij}$  is defined as

$$\Lambda_{ij} = \frac{v_j^L}{v_i^L} \exp - \left( \frac{\lambda_{ij} - \lambda_{ii}}{RT} \right) \quad (5.48)$$

where  $\lambda_{ij}$  is proportional to the i-j interaction, etc. Equations (6.1) and (6.2) show that one experimental point per binary,  $(x_1, \gamma_1, \gamma_2)_{\text{TorP}}$ , is sufficient to yield the Wilson parameters  $\Lambda_{12}$  and  $\Lambda_{21}$  for that system. However, it is found that the magnitude of both the Wilson parameters obtainable from equations (6.1) and (6.2) and the interaction energies obtainable from equation (5.48) depend on the composition point used to determine them.

Thus, two questions arise:

- a) What are the optimum Wilson parameters and/or interaction energies? i.e. which is the pair of parameters that will best predict the binary liquid phase activity coefficients?
- b) What is the effect of using non-optimum Wilson parameters or interaction energies on the activity coefficients predicted?

An attempt at answering these questions is made in the next sections.





## 6.2 Determination of Optimum Wilson Parameters and Interaction Energies

Mathematically, the equilibrium equation using Wilson's model can be presented as follows:

$$y_i = f(\Lambda_{ij}, \Lambda_{ji}, x_i, C)_P \quad (6.3)$$

where in equation (5.59), for example,  $C$  is the ratio of the vapor pressure to the total pressure.

Equation (6.3) can also be presented as

$$y_i = f[(\lambda_{ij} - \lambda_{ii}), (\lambda_{ji} - \lambda_{jj}), x_i, C]_P \quad (6.4)$$

by combining equation (5.48) with (6.3).

Two methods for the optimization of the parameters in these equations have been used in this work:

a) The first method is a finite optimum search technique.

Nineteen points in every binary (covering a liquid composition range of 0.05 to 0.95 mole percent at 0.05 intervals) are each used to yield a pair of Wilson parameters and interaction energies. Every pair of these parameters is then used to predict a range of vapor-phase composition. To make this possible, the activity coefficients and the temperature at every point, and the total pressure, have to be known. Each  $y$ -prediction is then compared to the experimental values by determining the standard deviation

$$D = \frac{\sum (y_{\text{pred.}} - y_{\text{obs.}})^2}{n-1} \quad (6.5)$$





Table 6.1

## Variation of Wilson Parameters and Interaction Energies

in Binary Methylcyclohexane(1) - Toluene(2)

Equilibrium Data by Quiggle, D., and M. Fenske<sup>33</sup>

System Pressure: 1 atm.

$X_{MCH}$ In Binary Mole %	System T °F	Wilson Parameter $\Lambda_{12}$	Wilson Parameter $\Lambda_{21}$	Interaction Energy ( $\lambda_{12}-\lambda_{11}$ ) cal/gm.mole	Interaction Energy ( $\lambda_{21}-\lambda_{22}$ ) cal/gm.mole	$\gamma_{YMCH}$ from Literature Data	$\gamma_{YTOL}$ Standard Deviation
0.050	229.19	1.9941	0.1300	-581.475	1584.727	0.0022	0.0003
0.100	227.40	0.3443	1.7769	724.434	-359.006	0.0001	0.0001
0.150	225.77	0.3200	1.7676	778.687	-355.101	0.0001	0.0001
0.200	224.40	0.5512	1.2981	374.448	-125.603	0.0000	0.0000
0.250	223.16	0.6734	1.1080	225.584	- 7.905	0.0001	0.0000
0.300	222.08	0.6257	1.1904	280.187	- 61.203	0.0000	0.0000
0.350	221.00	0.6333	1.1934	271.257	- 63.081	0.0000	0.0000
0.400	220.10	0.5685	1.2702	351.492	-109.456	0.0000	0.0000
0.450	219.20	0.5876	1.2661	327.005	-107.080	0.0000	0.0000
0.500	218.40	0.5779	1.2648	339.234	-106.313	0.0000	0.0000
0.550	217.67	0.6618	1.1448	238.499	- 32.161	0.0000	0.0000
0.600	216.95	0.6917	1.1182	205.683	- 14.684	0.0000	0.0000
0.650	216.41	0.7476	1.0401	147.928	39.104	0.0001	0.0000
0.700	215.87	0.8401	0.9369	61.214	116.833	0.0001	0.0001
0.750	215.42	0.5688	1.2581	351.079	-102.353	0.0001	0.0000
0.800	214.97	0.6062	1.1925	303.772	- 62.508	0.0001	0.0000
0.850	214.52	0.1072	2.0302	1591.463	-458.093	0.0005	0.0011
0.900	214.16	0.1127	2.0087	1554.277	-450.179	0.0005	0.0015
0.950	213.80	0.1233	1.9861	1487.726	-441.786	0.0005	0.0009



Table 6.2

## Optimum Wilson Parameters and Interaction Energies

for Some Binaries

Optimization by Technique (a) - Section 6.1

System	System Conditions	Wilson Parameter $\Lambda_{12}$	Wilson Parameter $\Lambda_{21}$	Interaction Energy $(\lambda_{12} - \lambda_{11})$ cal/gm.mole	Interaction Energy $(\lambda_{21} - \lambda_{22})$ cal/gm.mole
Phenol (1) - M.C.H. (2)	Isobaric: 1 atm.	1.1815	0.0884	69.206	1875.358
Phenol (1) - Toluene (2)	Isobaric: 1 atm.	1.0527	0.2697	155.279	953.367
M.C.H. (1) - Toluene (2)	Isobaric: 1 atm.	0.5779	1.2648	339.235	-106.313
Acetone (1) - Water (2)	Isothermal: 100°C	0.1237	0.5593	442.009	1537.752
Methanol (1) - Water (2)	Isothermal: 100°C	0.2377	1.4291	496.273	303.820
Acetone (1) - Methanol (2)	Isothermal: 100°C	0.4589	1.1860	38.689	412.227
Acetone (1) - Water (2)	Isobaric: 1 atm.	0.2977	0.3342	-164.869	1679.554
Methanol (1) - Water (2)	Isobaric: 1 atm.	0.3115	1.3289	241.043	354.809
Acetone (1) - Methanol (2)	Isobaric: 1 atm.	0.8452	0.6385	-315.874	719.156







where  $n$  is the number of points in the prediction range. The optimum pair of Wilson parameters (and interaction energies) is then the one which yields the minimum standard deviation  $|D|$ . Table 6.1 illustrates the range in the variations of the parameters with composition of the binary methylcyclohexane-toluene as an illustration.

Table 6.2 shows the values of the optimum Wilson parameters and optimum interaction energies obtained by this technique for several binaries. In predicting multicomponent equilibria it was assumed that the combination of the optimum binary parameters would yield the best multicomponent prediction.

- b) The second technique uses the concept of quasilinearization to predict the best values of the Wilson parameters  $\Lambda_{ij}$  and  $\Lambda_{ji}$  and/or the interaction energies  $(\lambda_{ij} - \lambda_{ii})$  and  $(\lambda_{ji} - \lambda_{jj})$ . The data needed are at least two totally described composition points. An initial guess of the parameters being optimized, henceforth referred to as  $A_{ij}$  and  $B_{ji}$ , is made, a range of  $y$  is predicted, and the prediction is compared to the available observed points. Although only two such points are needed, the wider the range of composition that the available information covers the more dependable the optimum Wilson parameters and/or interaction energies will be. A least squares criterion is applied to obtain a new set of  $A_{ij}$  and  $B_{ji}$ ,



a new y-profile is predicted and the process is continued until the difference between the parameters from two successive iterations is  $\leq 10^{-4}$ .

If  $A_{ij}^{(0)}$  and  $B_{ji}^{(0)}$  denote the initial guess points, then

$$\begin{aligned} y^{(1)} = & f^{(0)} + \left( \frac{\partial f}{\partial A_{ij}} \right)^{(0)} (A_{ij}^{(1)} - A_{ij}^{(0)}) \\ & + \left( \frac{\partial f}{\partial B_{ji}} \right)^{(0)} (B_{ji}^{(1)} - B_{ji}^{(0)}) \end{aligned} \quad (6.6)$$

where superscript (1) denotes values of  $A_{ij}$  and  $B_{ji}$  to be determined. In more general terms, the above equation can be written as

$$\begin{aligned} y^{(n+1)} = & f^{(n)} + \left( \frac{\partial f}{\partial A_{ij}} \right)^{(n)} (A_{ij}^{(n+1)} - A_{ij}^{(n)}) \\ & + \left( \frac{\partial f}{\partial B_{ji}} \right)^{(n)} (B_{ji}^{(n+1)} - B_{ji}^{(n)}) \end{aligned} \quad (6.7)$$

If a deviation is defined as E, then

$$\begin{aligned} E = & y_{\text{obs}} - \left( \frac{\partial f}{\partial A_{ij}} \right)^{(n)} A_{ij}^{(n+1)} - \left( \frac{\partial f}{\partial B_{ji}} \right)^{(n)} B_{ji}^{(n+1)} \\ & - f^{(n)} + \left( \frac{\partial f}{\partial A_{ij}} \right)^{(n)} A_{ij}^{(n)} + \left( \frac{\partial f}{\partial B_{ji}} \right)^{(n)} B_{ji}^{(n)} \end{aligned} \quad (6.8)$$

The known terms are defined as parameters in the equation

$$E = y - PA_{ij} - QB_{ji} - R \quad (6.9)$$





where

$$R = f^{(n)} - \left( \frac{\partial f}{\partial A_{ij}} \right)^{(n)} A_{ij}^{(n)} - \left( \frac{\partial f}{\partial B_{ji}} \right)^{(n)} B_{ji}^{(n)} \quad (6.10)$$

$$Q = \left( \frac{\partial f}{\partial B_{ji}} \right)^{(n)} \quad (6.11)$$

and

$$P = \left( \frac{\partial f}{\partial A_{ij}} \right)^{(n)} \quad (6.12)$$

squaring the error for absolute magnitudes

$$E^2 = (y - PA_{ij} - QB_{ji} - R)^2$$

Minimization of  $E^2$  corresponds to differentiating the above function with respect to  $A_{ij}$  and  $B_{ji}$  and setting the derivatives to zero

$$\frac{\partial E^2}{\partial A_{ij}} = -2P(y - PA_{ij} - QB_{ji} - R) \quad (6.13)$$

$$\frac{\partial E^2}{\partial B_{ji}} = -2Q(y - PA_{ij} - QB_{ji} - R) \quad (6.14)$$

Since these functions can be determined for as many prediction points as observed data are available, then

$$\sum \frac{\partial E^2}{\partial A_{ij}} = -[2Py + 2A_{ij} \sum P^2 + 2B_{ji} \sum PQ + 2 \sum PR] \quad (6.15)$$





$$\left[ \frac{\partial E^2}{\partial B_{ji}} \right] = - \left[ 2Qy + 2A_{ij} \left[ PQ + 2B_{ji} \left[ Q^2 + 2 \right] QR \right] \right] \quad (6.16)$$

setting the error functions to be zero, the two equations presented can be solved simultaneously to obtain new values of  $A_{ij}$  and  $B_{ji}$ .

The iterative procedure is stopped when the absolute difference between any two successive values of  $A_{ij}$  and  $B_{ji}$  is less than a certain tolerance (usually  $10^{-4}$ ).

Table 6.3 shows the optimum values of  $A_{ij}$  and  $B_{ji}$  for some binaries obtained by this method. A comparison of the figures in Tables 6.2 and 6.3 shows that the two techniques yield results quite different in magnitude. However, as will be seen later, the effect of this on subsequent predictions is slight.

Appendix I shows the expressions for the differentials and algebraic terms introduced in equations (6.6) to (6.16) inclusive. Appendix II shows the computer programs and the computer outputs used in the optimization studies.

### 6.3 Sensitivity of Y-Predictions to Non-Optimal Wilson Parameters and Interaction Energies

To study the effect of using non-optimal parameters on the eventual vapor-phase composition predictions, it was decided to use equation (5.59) to predict isobaric ternary acetone-methanol-water vapor compositions at



Table 6.3

Optimum Wilson Parameters and InteractionEnergies for Some Binaries

Optimization by Technique (b) - Section 6.1

System	System Conditions	Wilson Parameters		Interaction Energies ( $\lambda_{12} - \lambda_{11}$ ) cal/gm.mole	Interaction Energies ( $\lambda_{21} - \lambda_{22}$ ) cal/gm.mole
		$\Lambda_{12}$	$\Lambda_{21}$		
Acetone(1)-Methanol(2)	Isobaric: 1 atm.	0.7173	0.8024	-235.73	597.42
Methanol(1)-Water(2)	Isobaric: 1 atm.	0.2219	1.4280	551.34	304.49
Acetone(1)-Water(2)	Isobaric: 1 atm.	0.1169	0.3908	570.69	1578.94

System

System Conditions

Wilson  
Parameters  
 $\Lambda_{12}$ Wilson  
Parameters  
 $\Lambda_{21}$ Interaction  
Energies  
( $\lambda_{12} - \lambda_{11}$ )Interaction  
Energies  
( $\lambda_{21} - \lambda_{22}$ )

cal/gm.mole

cal/gm.mole





1 atmosphere using:

- a) optimum Wilson parameters obtained by technique (a) using isobaric binary data at 1 atmosphere. The same Wilson parameters are used regardless of the temperature of the ternary point.
- b) optimum interaction energies obtained by technique (a) using isobaric binary data at 1 atmosphere. A new set of  $\Lambda$ 's is calculated from equations (5.48) and (5.49) at every ternary prediction point.
- c) optimum Wilson parameters obtained by technique (a) using isothermal binary data at 100°C. Effect of temperature here is completely neglected.
- d) optimum interaction energies obtained by technique (a) using isothermal data at 100°C. A new set of  $\Lambda$ 's is calculated from equations (5.48) and (5.49) at every new ternary temperature.
- e) optimum interaction energies obtained by technique (b) using isobaric data at 1 atmosphere. A new set of  $\Lambda$ 's is calculated at every prediction point.

The values for these parameters are reported in Table 6.4. In every one of the above cases the y-predictions were compared to the literature values<sup>34,35</sup> and standard deviations computed.



Table 6.4

Effect of Using Non-Optimum Wilson Parameters and Interaction Energies  
on Predicting Vapor Phase of Acetone-Methanol-Water System at P = 1 atm.

Standard Deviation of  $Y_i$   
Compared to Isobaric Data<sup>34,35</sup>  
(1 atm.)

Conditions  
of  
Binaries

$\sigma_{Y_{\text{Acetone}}}$   $\sigma_{Y_{\text{Methanol}}}$   $\sigma_{Y_{\text{Water}}}$

## Optimization Technique (a)

Acetone (1)-Water(2) Isobaric 0.2977 0.3342 0.2467 0.2171 0.1956  
Methanol(1)-Water(2) 1 atm. 0.3115 1.3289  
Acetone(1)-Methanol(2)\* 0.8452 0.6385

Acetone(1)-Water(2) Isobaric  
Methanol(1)-Water(2) 1 atm.  
Acetone(1)-Methanol(2)+

Acetone(1)-Water(2) Isothermal 0.1237 0.5593  
Methanol(1)-Water(2) 1000C 0.2377 1.4291  
Acetone(1)-Methanol(2)\* 0.4589 1.1860

Acetone(1)-Water(2) Isothermal  
Methanol(1)-Water(2) 1000C  
Acetone(1)-Methanol(2)+

## Optimization Technique (b)

Acetone(1)-Water(2) Isobaric  
Methanol(1)-Water(2) 1 atm.  
Acetone(1)-Methanol(2)+

\* Effect of changing temperatures neglected  
+ New  $\Lambda$ 's calculated at every temperature





A conclusion that can be reached from the results in Table 6.4 is that the interaction energies have no temperature dependency, i.e., once the optimum values for a binary have been calculated they can be used with confidence to predict vapor equilibria covering a wide range of temperatures. Moreover, interaction energies obtained from binaries under some conditions can be used to predict equilibria at reasonably removed conditions, e.g., the optimum interaction energies obtained from the binaries at 100°C can be used without a great loss in accuracy to predict vapor phase compositions in the isobaric (1 atm.) ternary where the temperature ranges from 58.2°C to 70.0°C.

The Wilson parameters on the other hand are strongly temperature dependent. Table 6.4 shows that regardless of the conditions in the binaries, their accuracy in prediction is poor when the temperature effect is not taken into consideration.

The two optimization techniques produce interaction energies and Wilson parameters that are at times quite different. However, as Table 6.4 shows, these different optimum values predict the ternary data equally well.





VII. STUDY OF MULTICOMPONENT DISTILLATION COLUMNS  
WITH THE GENERALIZED COMPUTATIONAL ROUTINE

7.1 Detailed Calculational Procedure

The procedure presented in Section 4.5 for the study of distillation columns can now be outlined in detail as follows:

- 1) Assume initial temperature, vapor, and liquid profiles.
- 2) Use any of the following models for the determination of the vaporization constants  $K_{ij}$ :
  - a) Polynomial temperature function if the behavior of the components in the system can be considered independent of concentration
  - b) Chao-Seader correlation for the range of compounds for which it is applicable. In this correlation,  $K_{ij}$  is a function of both temperature and composition
  - c) The Wilson equation for the determination of liquid-phase activity coefficients coupled with the use of the simplified equilibrium equation (5.59).

For those cases such as (b) and (c) where the  $K_{ij}$ 's are a function of both temperature and composition in the column, the composition profile is calculated for the first iteration only by the use of a polynomial or an ideal- $K_{ij}$  subroutine. The latter subroutine is obtained from the Chao-Seader model by assuming the liquid phase activity



coefficients to be equal to the vapor phase fugacity coefficients.

- 3) Apply the tridiagonal matrix method and the modified Gauss elimination algorithm to calculate a liquid composition profile.
- 4) Calculate a new temperature profile applying Muller's quadratic root method.
- 5) Calculate the new vapor and liquid profiles by solving the energy balance equations. The component vapor and liquid enthalpies can be obtained by any of the following methods:
  - a) Polynomial fits of the enthalpies with temperature such as in hydrocarbons up to  $C_{10}$ .
  - b) Chao-Seader enthalpy correlation for the hydrocarbons where the model is applicable.
  - c) Component enthalpies from the literature<sup>22</sup> with the necessary corrections to take the mixing effects into consideration.
- 6) Return to step (2) using the newly obtained  $T_j$ 's and  $V_j$ 's and repeat the procedure until the sum over the column of the squares of the temperature differences between two successive iterations is less than a certain value (usually  $0.01N$  where  $N$  is the number of stages).

The computer flow diagram for both composition-dependent  $K_{ij}$  routines is shown in Figure 7.1.

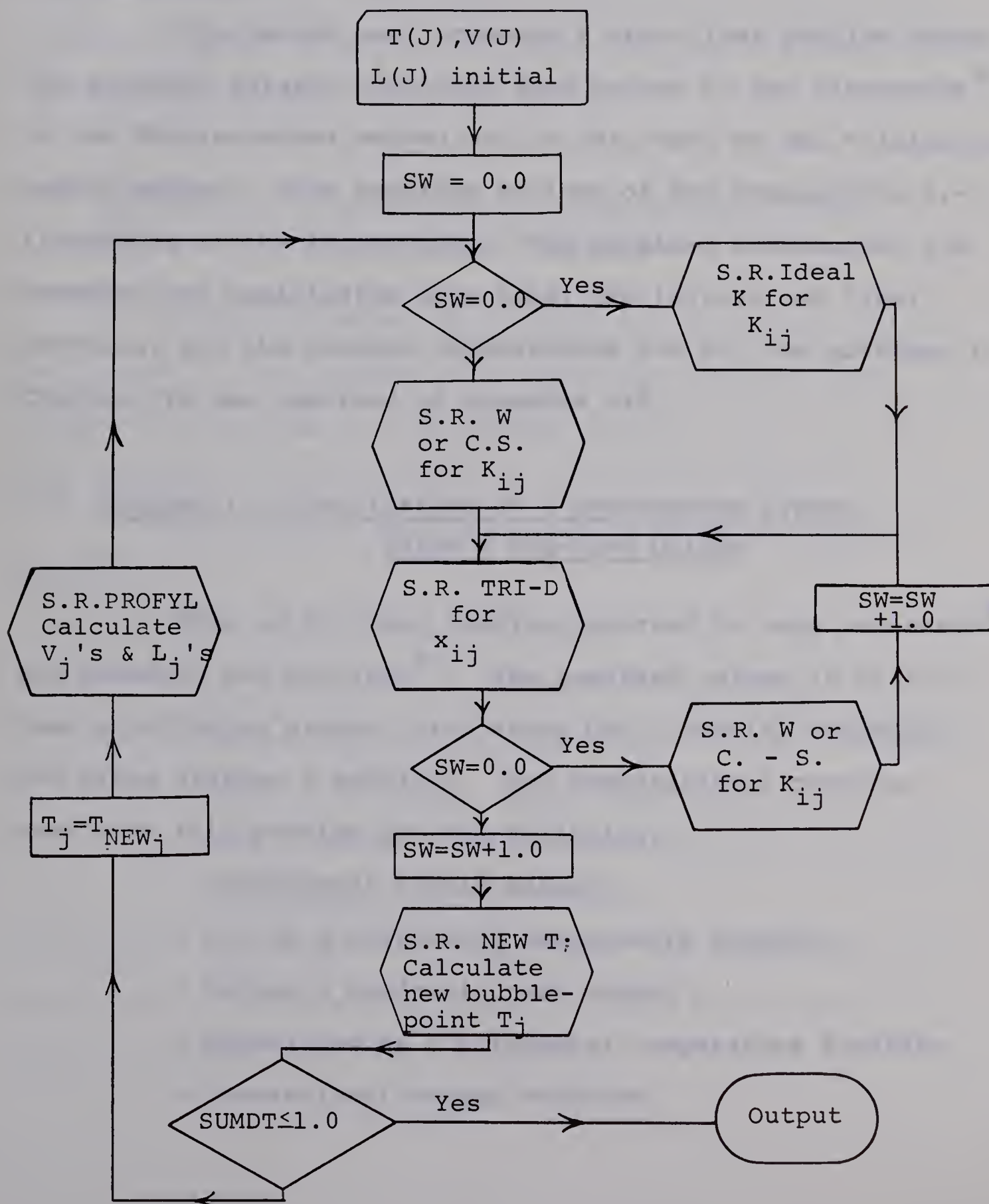






Figure 7.1

Flow Diagram : S.R. Ideal K and S.R. Wilson (W)  
or Chao-Seader (C.S.)





The first part of this chapter presents two test problems. These problems were solved in the literature using the same method outlined above and the results were available for comparison.

The second part presents a stabilizer problem where the material balance equations were solved in the literature<sup>39</sup> by the Thiele-Geddes method and in this work by the tridiagonal matrix method. This provides an idea of the comparative efficiencies of the two methods. The detailed statements, the enthalpy and equilibrium data used, the initial and final profiles, and the product compositions for all the problems in Chapter VII are reported in Appendix III.

## 7.2 Problem I: Distillation of a Hydrocarbon System Using a One-Feed Column

This is the same problem reported by Wang and Henke<sup>26</sup> and Amundson and Pontinen<sup>23</sup>. The one-feed column is of sixteen equilibrium stages, with stage one a partial condenser and stage sixteen a reboiler. The computational routines used with this problem are the following:

- Tridiagonal matrix method
- $K_{ij}$  as a polynomial temperature function
- Muller's quadratic root method
- Enthalpies as a polynomial temperature function
- Conventional energy balances





The results from this work duplicated those of Wang and Henke<sup>26</sup> in four iterations as compared to the reported seven. This improvement is due to the normalization of the liquid composition. Total object time for this problem was fourteen seconds on an IBM 7040 computer. This is equivalent to 0.04 sec/component/stage/iteration.

### 7.3 Problem II: Distillation of a Hydrocarbon System Using a Complex Column

This problem was also studied by Wang and Henke<sup>26</sup> and Lyster<sup>25</sup>. The system to be separated contains eleven hydrocarbon components. The column uses two feeds and two side streams, with a total of 21 equilibrium stages.

The routines used with this problem are the following:

- Tridiagonal matrix method
- $K_{ij}$  as a polynomial function of temperature
- Muller's quadratic root method for the determination of the bubble point temperature
- Enthalpies as a polynomial temperature function
- Conventional energy balances

The program converged in 10 iterations, the computation time being 0.036 secs/component/stage/iteration and the total object time being 1 min. and 23 seconds.





#### 7.4 Problem III: Use of the Chao-Seader Correlation with Problem II

Since one of the equilibrium and enthalpy models specifically applicable to many hydrocarbon systems is the Chao-Seader correlation, it was decided to use the Chao-Seader correlation for equilibrium and enthalpy data with problem II using the same computational procedure as outlined above. The program converged in 7 iterations with a computation time of 0.08 secs/component/stage/iteration and a total object time of 2 minutes and 14 seconds.

Since the only difference between problems II and III is the method of obtaining the equilibrium and enthalpy data, it can be seen from the computation times that the Chao-Seader correlation takes almost 3 times as long as the polynomial model in yielding equilibrium and enthalpy data. The number of iterations in this problem was 7. This program shows, however, that the Chao-Seader correlation can be successfully used with a complex column (more than one feed and two product streams).

Appendix V presents the detailed computer program for problem III as an example of the programming used with the problems in this chapter.



#### 7.5 Problem IV: Use of Tridiagonal Matrix and Muller Methods with a Stabilizer Column

Tatuch<sup>39</sup> solved this stabilizer problem using the Thiele-Geddes method to obtain composition profiles. The same problem was solved in this work using the tridiagonal matrix method.

The routines used with this problem were as follows:

- Tridiagonal matrix method
- Chao-Seader  $K_{ij}$ 's
- Muller's quadratic method
- Chao-Seader enthalpies
- Conventional enthalpy balances

The program converged in 10 iterations with a computation time of 0.12 secs/iteration/component/stage. The total object time was 5 minutes and 27 seconds compared to 3 minutes and 55 seconds reported by Tatuch<sup>39</sup>. However, these object times are not strictly comparable since Tatuch<sup>39</sup> does not report the initially assumed profiles.







## VIII. EXTRACTIVE DISTILLATION: PART I

The work done on the distillation of hydrocarbon systems presented above showed that the tridiagonal matrix method is adequate for the simultaneous solution of the material and energy balance equations in complex columns (more than one feed and more than two product streams). This work also showed that the quadratic fit algorithm for the determination of the bubble point vector across a column (the Muller method) is adequate. The Wilson equation in Section 6.3 was shown to be capable of predicting multicomponent vapor-liquid equilibria using data obtained from the binary systems only. It was thus decided to study some extractive distillation columns using these computational routines. All extractive distillation columns are two-feed columns. The systems handled in these columns always show large deviations from Raoult's law so that the application of these routines to extractive distillation would be a good test for their versatility. The flow diagram for the computational procedure has been presented in Section 7.1 and Figure 7.1.

### 8.1 Problem V: Extractive Distillation of the System Methylcyclohexane (MCH)-Toluene with Phenol

The problem is to optimally separate 100 moles/unit time of a 50-50 MCH-toluene mixture. The binary separation of MCH and toluene is extremely difficult since MCH boils at  $101^{\circ}\text{C}$  and toluene boils at  $110.8^{\circ}\text{C}$ .



Accordingly phenol is used as the extractive agent since it satisfies all the properties specified for a solvent in Chapter III.

Problem V was studied by Smith<sup>19</sup> where he presented the first iteration in calculating the number of stages required to achieve a specified separation. Since the physical configuration of the column is necessary prior to using the programs developed in this work, a preliminary study was necessary to determine the stages at which the solvent and fresh feed streams should be introduced.

The number of specifications required for this column is  $2C + 2N + 12$ . The choice made from the  $2C + 2N + 15$  specifications reported in Section 3.6 is the following:

Pressure in N-stages		N	
Pressure in condenser			1
Pressure and heat leak in reflux divider			2
Heat leak in N-1 stages		N -	1
Condenser load			1
Total number of stages			1
Fresh feed composition temperature and rate	C	+	2
Fresh feed location			1
Solvent feed composition temperature and rate	C	+	2
Solvent feed location			1
Rate of overhead product			1
L/D ratio			1
			<hr/>
			$2C + 2N + 12$

Figure 8.1 shows the result of the study relating to the feed introduction stages.





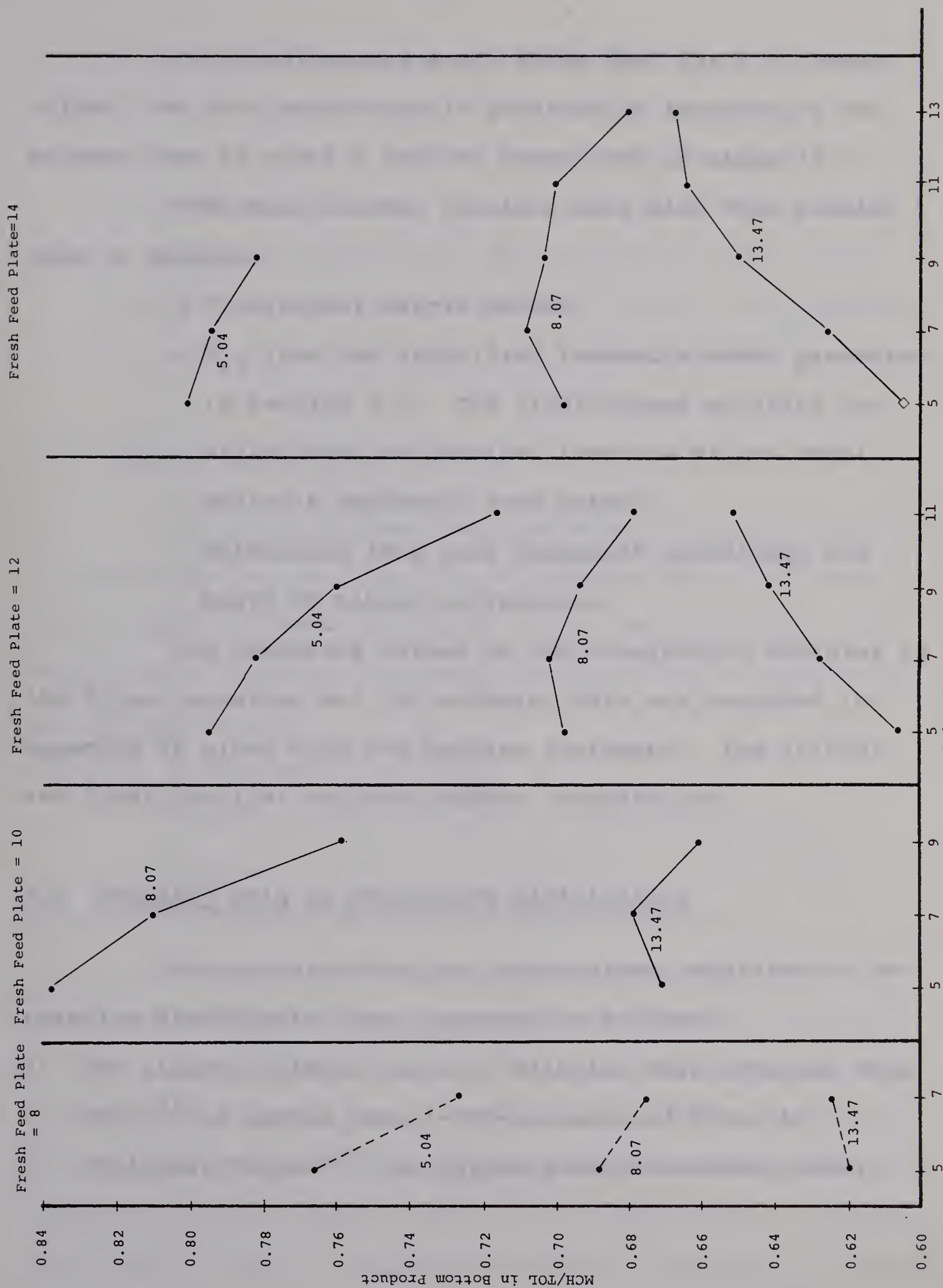


Figure 8.1 Study to Locate Solvent and Fresh Feed Plates

Total plates = 21

Parameter = L/D





This preliminary study shows that for a 21 stage column, the best separation is obtained by introducing the solvent feed in stage 5 and the fresh feed in stage 14.

The computational routines used with this problem were as follows:

- Tridiagonal matrix method
- $K_{ij}$  from the simplified Prausnitz model presented in Section 5.5. The liquid-phase activity coefficients are obtained from the Wilson model
- Muller's quadratic root method
- Enthalpies from pure component enthalpies and heats of mixing corrections.

The optimized values of the interaction energies in the Wilson equation and the enthalpy data are reported in Appendix IV along with the problem statement, the initial and final profiles and the product compositions.

## 8.2 Enthalpy Data in Extractive Distillation

The enthalpy data for the systems separated by extractive distillation were computed as follows:

- 1) The binary infinite-heats of dilution were obtained from Smith<sup>19</sup> for system phenol-MCH-toluene and from the "Critical Tables"<sup>20</sup> for system acetone-methanol-water.



- 2) Equation (5.65) was used to obtain partial molar heats of solution at the compositions of the stages
- 3) Equation (5.63) was used to calculate enthalpies of the liquid phase. Ideality of the vapor phase was assumed. The equations representing the variation of the enthalpies of the ideal vapor and liquid phases with temperature were derived from the Data Book on Hydrocarbons<sup>22</sup>.

### 8.3 Optimization of the Column

With this information available, the optimization of the operation variables of the column such as reflux ratio and solvent and fresh feed rates could now be studied. The separation efficiency was characterized by one of the following two parameters:

- Recovery of toluene
- Ratio of MCH/toluene in the bottom product

Figure 8.2 shows the dependence of MCH/toluene ratio in the bottoms on rate of solvent feed and  $L_1/D$  ratio. With increasing  $L_1/D$  ratio and increasing solvent rate, the purity of the bottom product (the toluene product) improves.

The dependence of the recovery of toluene on the same two variables is shown in Figure 8.3. We can note from this figure that for a fixed  $L_1/D$  ratio, a higher recovery is sometimes possible with a lower solvent feed rate. To show this effect clearly, Figure 8.4 shows the variation of solvent







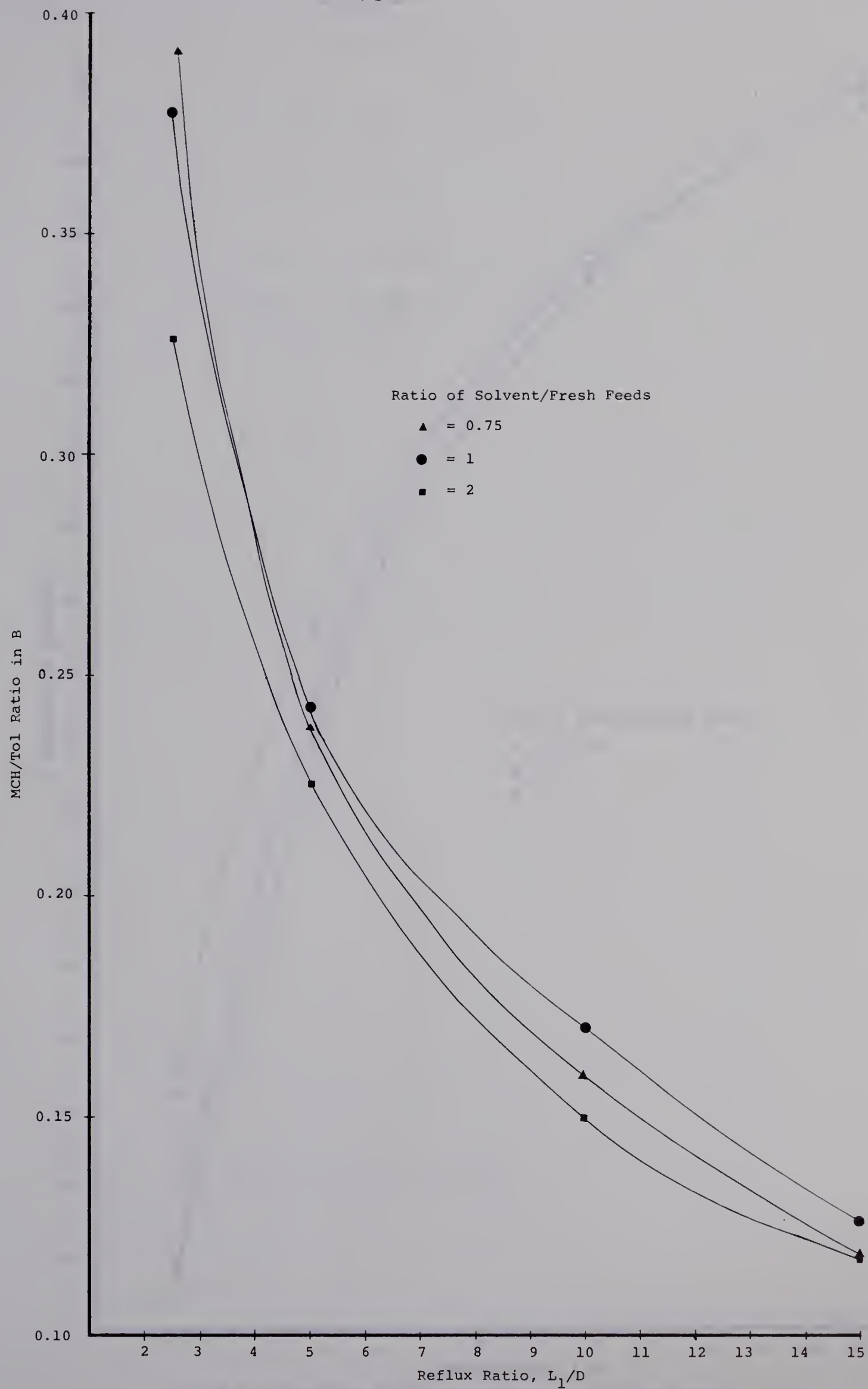


Figure 8.2 Variation of MCH/Tol Ratio with the Reflux Ratio



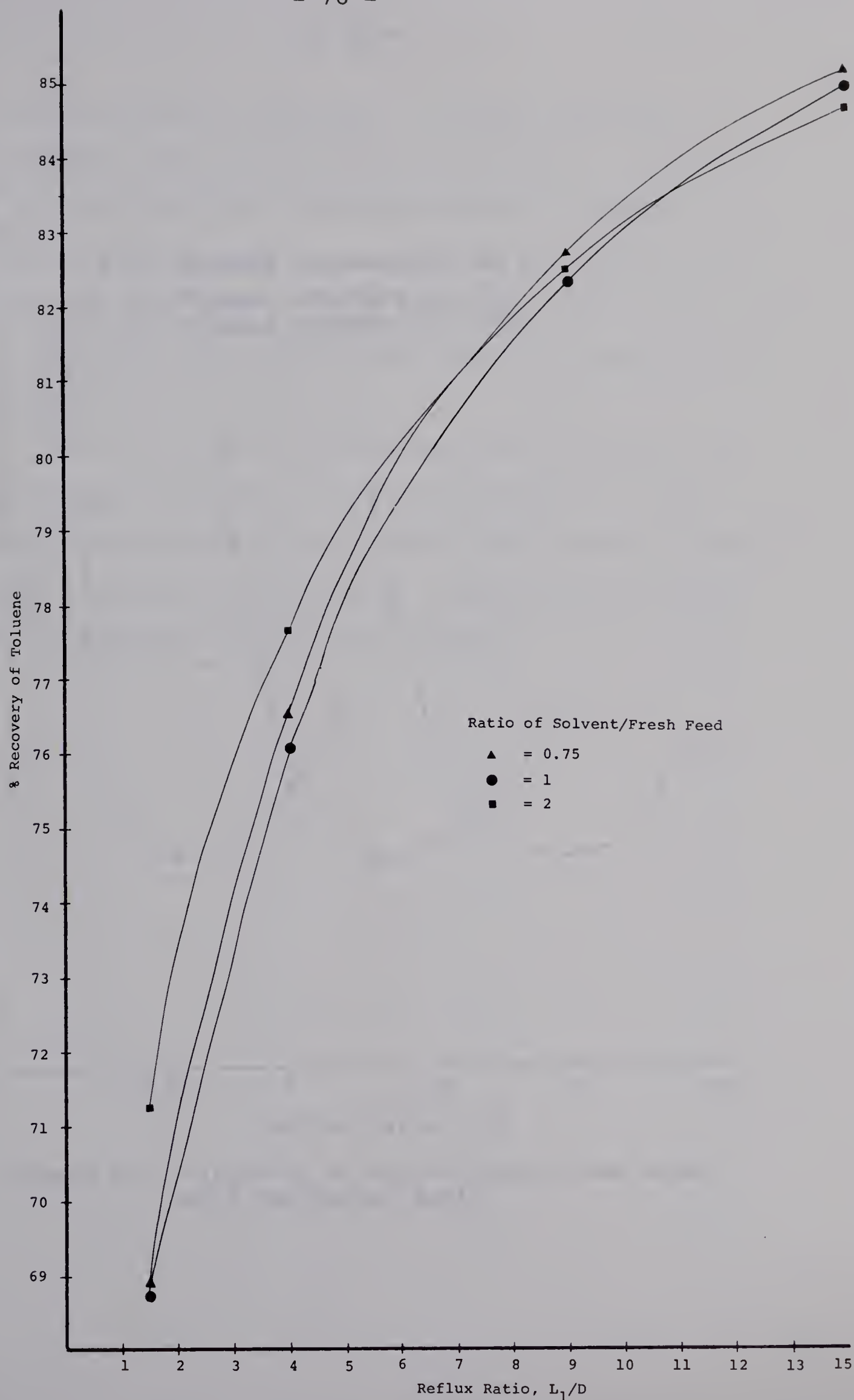


Figure 8.3 Variation of Toluene Recovery with Reflux Ratio



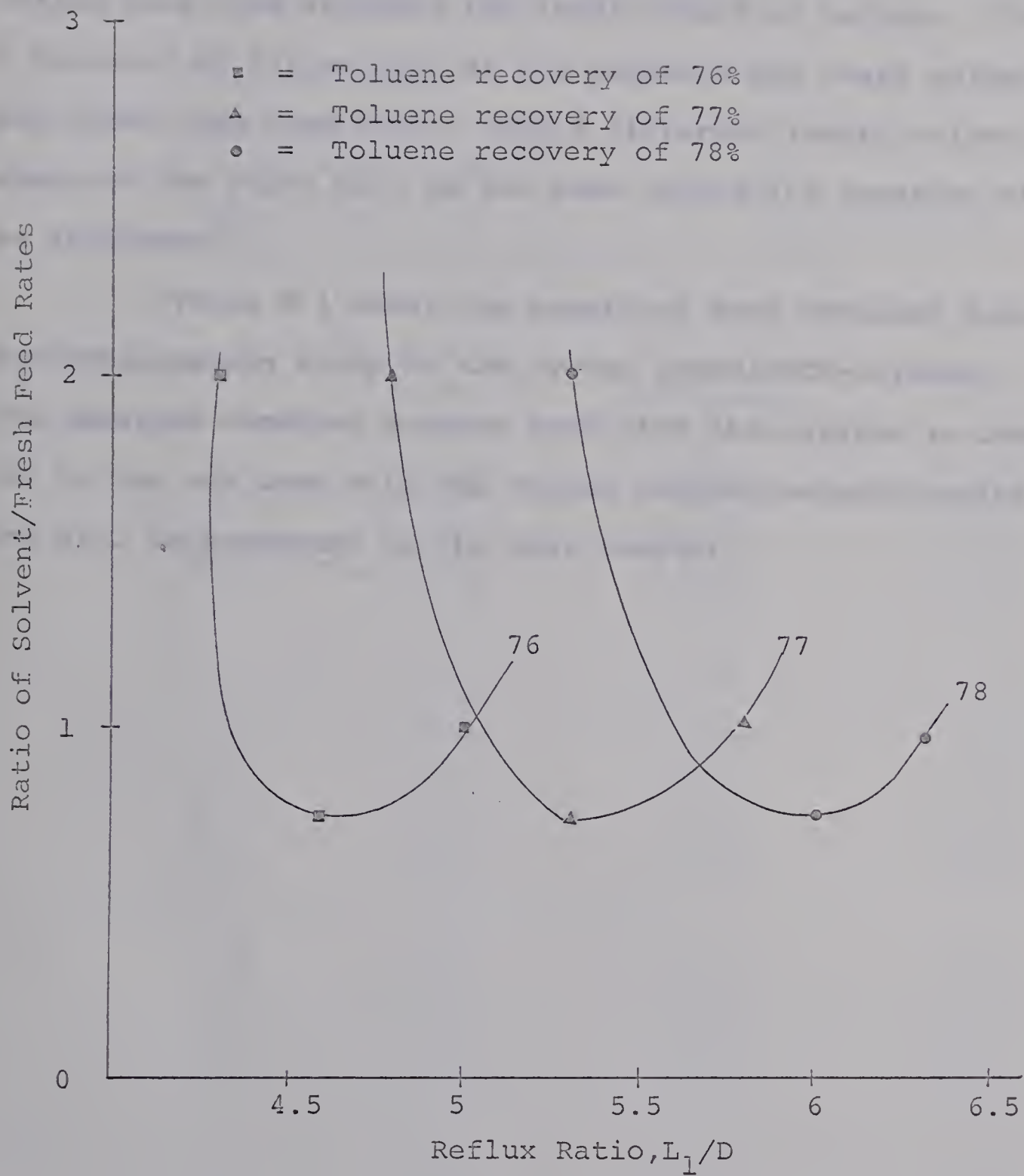


Figure 8.4 Variation of Solvent/Fresh Feed Rates with the Reflux Ratio





feed rate with the  $L_1/D$  ratio for toluene recoveries of 76, 77 and 78%. This figure shows that there is a particular reflux rate that requires the least amount of solvent. For a recovery of 77%, an  $L_1/D$  of 5.3 requires the least solvent per fresh feed rate ratio. For a different length column, the shape of the curve will be the same though its location will be different<sup>10</sup>.

Table 8.1 shows the numerical data obtained from the optimization study of the system phenol-MCH-toluene. The detailed computer program used with this system is identical to the one used with the system acetone-methanol-water and will be presented in the next chapter.



Table 8.1

Numerical Results for the Optimization  
of the System Phenol-MCH-Toluene

No. of stages = 21  
Solvent Feed Location = 5  
Fresh Feed Location = 14  
Fresh Feed Rate,  $F_1$  = 100 moles/U.T.  
Phenol Concentration in D  $\leq$  0.002

$F_2/F_1$	$L_1/D$	MCH/Tol in Bot	% Recovery of Toluene	% Phenol in D
0.75	2.5	0.3919	68.95	0.0004
	5.0	0.2385	76.55	0.0001
	10.0	0.1602	82.70	0.0000
	15.0	0.1187	85.20	0.0000
	20.0	0.0987	86.44	0.0000
	25.0	0.0802	87.25	0.0000
1.0	1.5	0.4795	64.32	0.0015
	2.0	0.4243	66.62	0.0008
	2.5	0.3782	68.78	0.0005
	5.0	0.2432	76.08	0.0002
	10.0	0.1700	82.37	0.0001
	15.0	0.1268	84.97	0.0000
	20.0	0.1038	86.26	0.0000
	25.0	0.0900	87.02	0.0000
1.5	1.5	0.4497	65.47	0.0019
	2.0	0.3967	67.89	0.0011
	2.5	0.3550	69.99	0.0007
	5.0	0.2361	76.86	0.0002
	10.0	0.1550	82.46	0.0001
	15.0	0.1403	84.76	0.0001
2.0	1.5	0.4180	66.31	0.0020
	2.0	0.3665	69.07	0.0012
	2.5	0.3277	71.24	0.0008
	5.0	0.2244	77.66	0.0003
	10.0	0.1512	82.57	0.0001
	15.0	0.1173	84.66	0.0001





## IX. EXTRACTIVE DISTILLATION: PART II

### 9.1 Problem VI: Extractive Distillation of Acetone-Methanol

The possibility of using the computational routines developed in this work to study and optimize extractive distillation was shown in Chapter VIII on the phenol-methylcyclohexane-toluene system. Since, however, it was not possible to rigorously verify the results obtained, it was decided to

a) simulate

b) optimize

an existing industrial column.

Chemcell (1963) Ltd. provided us with all the required information for the study of their acetone-methanol extractive distillation tower with water as the solvent.

This information is presented in Figure 9.1 and Table 9.1 presented below.

### 9.2 Simulation of the Industrial Column

In the simulation of an existing industrial separation column, the first attempt is to measure the operating conditions and performance. This will yield component balances around the column when coupled with accurate analyses on the ingoing and outgoing streams. The next step is to vary the number of stages in every section in the column until the overhead and bottoms compositions are duplicated.



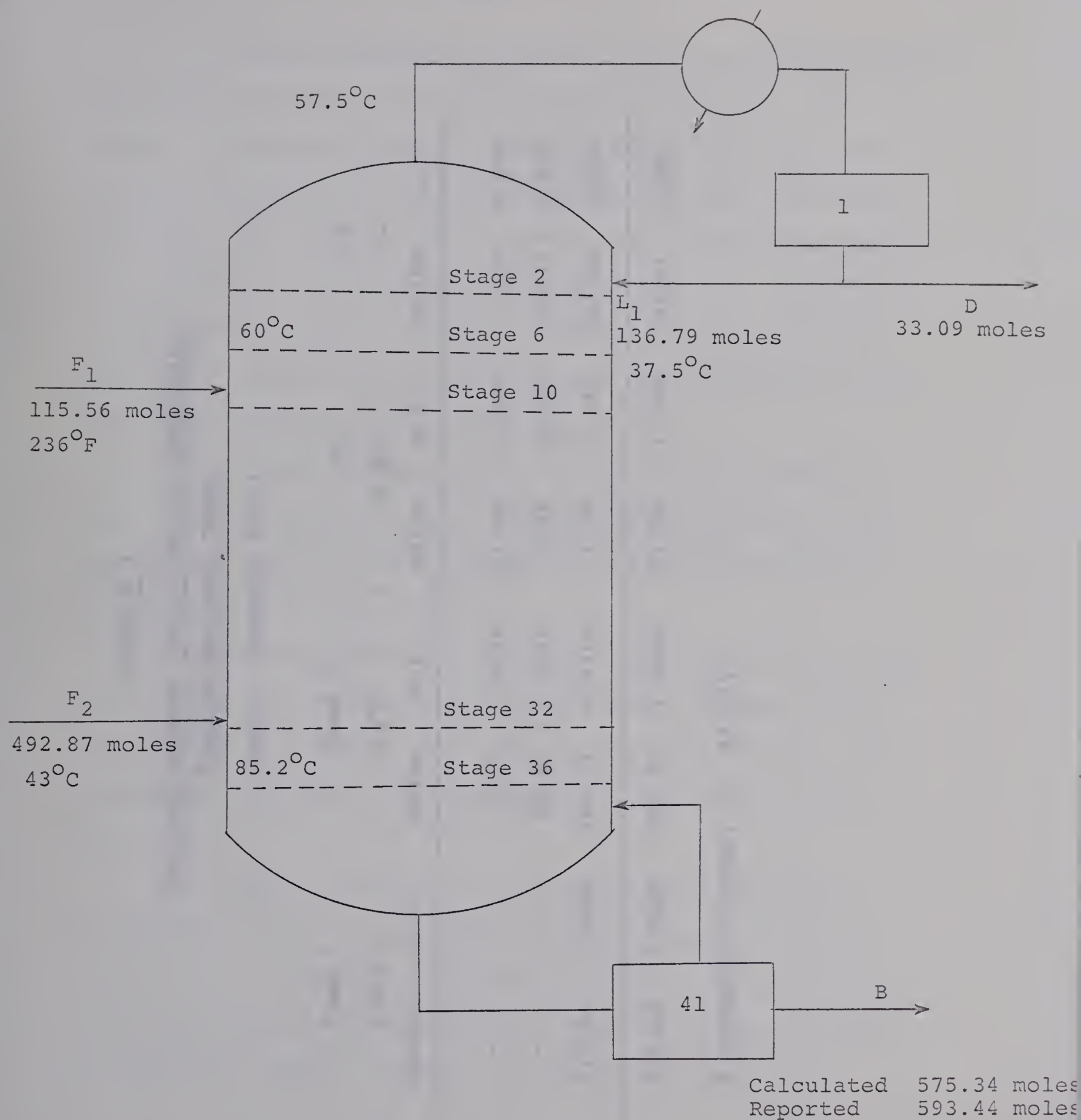


Figure 9.1 Diagram of Industrial Acetone-Methanol Tower  
(Chemcell Ltd.)



Table 9.1

Feed and Product Conditions in Industrial

Acetone-Methanol Tower

(Data: Chemcell Ltd.)

Component	Feed 1		Feed 2		D		B	
	moles	m.f.	moles	m.f.	moles	m.f.	moles	m.f.
Temperature	236°F		43°C		37.5°C		—	
Acetone	—	—	35.38	0.0718	31.68	0.957	5.19	0.009
Methanol	—	—	47.92	0.0972	0.06	0.002	20.77	0.035
Water	115.56	1.0000	409.57	0.8310	1.35	0.041	567.45	0.956
Total	115.56	1.0000	492.87	1.0000	33.09	1.000	593.41	1.000

% methanol recovery = 43.34%





However, obtaining a perfect material balance around the column for every component is almost impossible with the chemical system under study. This is due to the fact that laboratory analyses for acetone-methanol mixtures are rather difficult. As a result, the two feed rates and their compositions and the overhead rate and composition were assumed to be the correct ones. A material balance around the column with these values showed that the reported bottoms flow rate was 3.15% higher than the calculated one.

The flow diagram shown in Figure 7.1 is the one used with this problem also. The specified degrees of freedom are the same as those specified for the optimization of the phenol-MCH-toluene system.

The variables whose influence on the simulation was studied were the total number of equilibrium stages and the locations of the feeds. The other specifications were held constant at the same values as reported in Figure 9.1 and Table 9.1.

Table 9.2 shows the results from the simulation and compares them to the reported information on the industrial column. The problem statement, initial and final profiles and product compositions are reported in Appendix IV. The detailed computer program is reported in Appendix V.



Table 9.2

## Data on Simulation of Acetone-Methanol-Water Tower

$F_1$  flow rate = 115.56 moles  
 $F_2$  flow rate = 492.87 moles  
 D flow rate = 33.09 moles

Total Number of Equilibrium Stages (Condenser = 1)	Total Column Efficiency	$F_1$ Stage	$F_2$ Stage	Acetone m.f. in D	Methanol m.f. in D	Water m.f. in D
25	0.609	9	20	0.9637	0.0055	0.0308
25	0.609	8	20	0.9521	0.0164	0.0315
22	0.536	8	18	0.8990	0.0816	0.0194
22	0.536	7	18	0.8996	0.0761	0.0244
22	0.536	6	18	0.9008	0.0674	0.0317
Reported for 41 non-equilibrium stages, $F_1$ at stage 10, $F_2$ at stage 32						
				0.957	0.002	0.041





### 9.3 Activity Coefficient Predictions with the Wilson Model at Low Concentrations

As was mentioned in Chapter VII, the convergence criterion ordinarily set for distillation problems is that the sum over the column of the squares of the temperature differences between two successive iterations be less than 0.01 times  $N$ , where  $N$  is the number of stages. In this thesis, the convergence criterion set for  $\sum_{j=1}^N (\Delta T^2)$  was 1.0 or less. This criterion was generally met with the phenol-MCH-toluene system studied in the preceding chapter. With the acetone-methanol-water system, however, it was not possible at first to bring  $\sum_{j=1}^N (\Delta T^2)$  below a certain minimum value, often close to 10.0. When  $\sum_{j=1}^N (\Delta T^2)$  reached that point, it would increase again for a few iterations, and oscillations resulted. This trend to oscillate occurred in all cases except when the solvent feed rate and the reflux ratio were very low. In examining this difficulty several parameters that were thought relevant, including  $\sum_{j=1}^N (\Delta T^2)$  were plotted vs. the iteration in the manner of Figure 9.2. From this graph it was noticed that the trend in the variation of  $\sum_{j=1}^N (\Delta T^2)$  was closely followed by a similar trend in the bottom composition of acetone, component 1, and was not followed by any of the other plotted variables. It was thus hypothesized that as the concentration of acetone in the bottoms decreased, which would be the expected trend toward convergence acetone being the top product, the ability



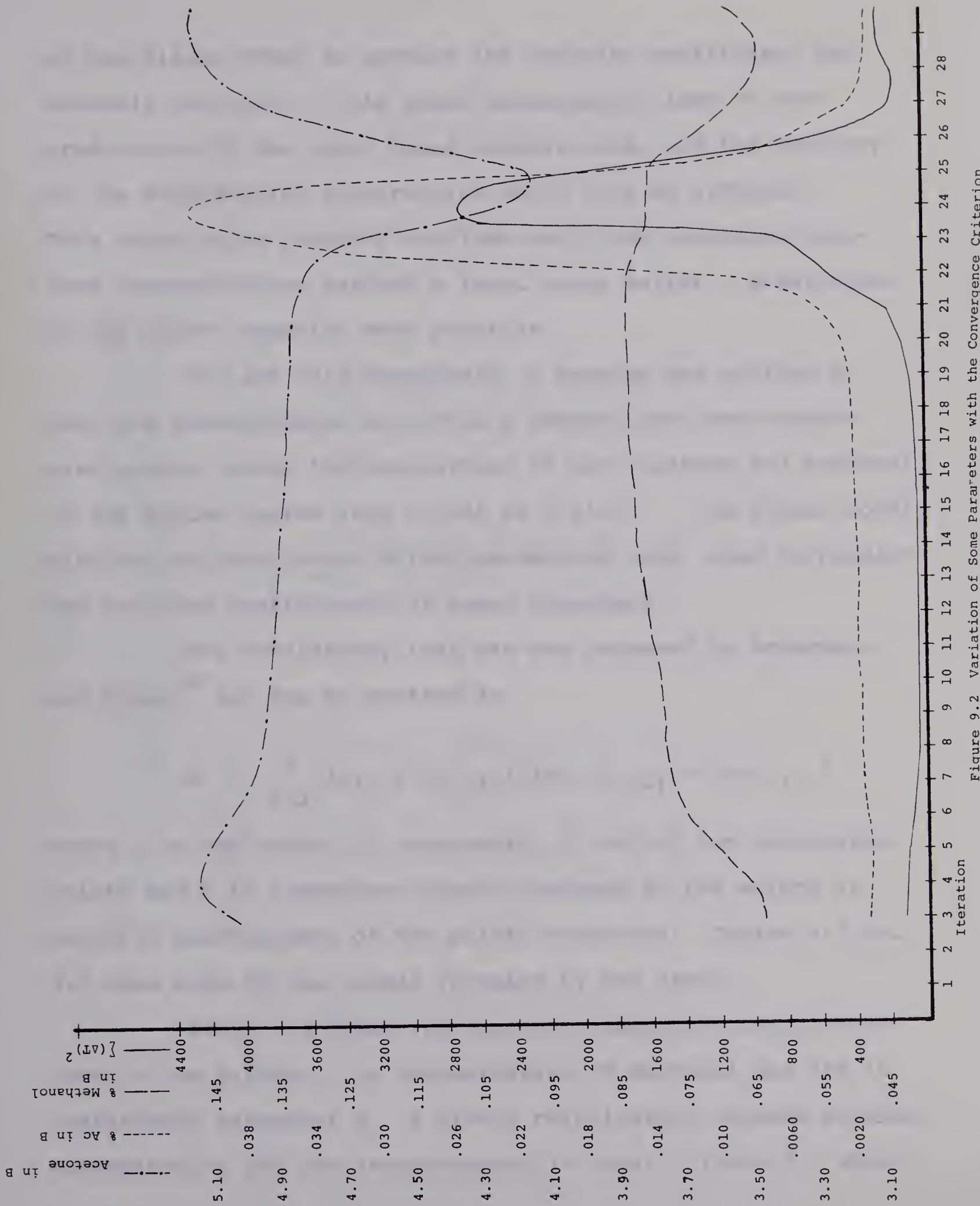


Figure 9.2 Variation of Some Parameters with the Convergence Criterion





of the Wilson model to predict its activity coefficient was severely curtailed. This would consequently lead to poor predictions of the vapor phase compositions, and the accuracy of the bubble-point temperatures would thus be affected. This trend would probably continue until the increasing acetone concentrations reached a level where better  $\gamma$  predictions by the Wilson equation were possible.

To test this hypothesis, a program was written to test the thermodynamic consistency between each two successive points, where the composition of both acetone and methanol in the system varied from 0.0005 to 0.5120. The Wilson model, with the optimum binary Wilson parameters, was used to predict the activity coefficients of every component.

The consistency test was one proposed by McDermott and Ellis<sup>40</sup> and can be written as

$$D = \sum_{i=1}^C (x_{ij} + x_{i,j+1}) (\log \gamma_{i,j+1} - \log \gamma_{i,j})$$

where C is the number of components, j and j+1 two successive points and D is therefore directly related to the errors in activity coefficients of the points concerned. Tables 9.3 and 9.4 show some of the trends revealed by the study.

Table 9.3 shows (at constant concentrations of acetone in the ternary) the concentration of methanol and the inconsistency parameter D. A direct relationship between methanol concentration and the inconsistency is clear. Table 9.4 shows





Table 9.3

Variation of Thermodynamic Inconsistency Parameter  
With X-Methanol in Acetone-Methanol-Water

$X_{\text{Acetone}}$	$X_{\text{Methanol}}$	Inconsistency Parameter	$X_{\text{Acetone}}$	$X_{\text{Methanol}}$	Inconsistency Parameter
0.0005	0.0005	+0.764 * E-08	0.2560	0.0005	-0.555 * E-08
0.0005	0.0010	-0.326 * E-08	0.2560	0.0010	+0.134 * E-07
0.0005	0.0020	-0.103 * E-07	0.2560	0.0020	-0.131 * E-07
0.0005	0.0040	-0.691 * E-07	0.2560	0.0040	-0.497 * E-07
0.0005	0.0080	-0.571 * E-06	0.2560	0.0080	-0.351 * E-06
0.0005	0.0160	-0.427 * E-05	0.2560	0.0160	-0.266 * E-05
0.0005	0.0320	-0.297 * E-04	0.2560	0.0320	-0.189 * E-04
0.0005	0.0640	-0.184 * E-03	0.2560	0.0640	-0.120 * E-03
0.0005	0.1280	-0.942 * E-03	0.2560	0.1280	-0.644 * E-03
0.0005	0.2560	-0.374 * E-02	0.2560	0.2560	-0.268 * E-02
0.0005	0.5120	+0.529 * E-01	0.2560	0.5120	+0.107 * E-01

1  
∞  
∞  
1



Table 9.4

Variation of Thermodynamic Inconsistency Parameter  
with X-Acetone in Acetone-Methanol-Water

$X_{\text{Acetone}}$	$X_{\text{Methanol}}$	Inconsistency Parameter	$X_{\text{Acetone}}$	$X_{\text{Methanol}}$	Inconsistency Parameter
0.0005	0.0005	+0.764 * E-08	0.0005	0.2560	-0.374 * E-02
0.0010	0.0005	+0.468 * E-08	0.0010	0.2560	-0.373 * E-02
0.0020	0.0005	+0.392 * E-08	0.0020	0.2560	-0.373 * E-02
0.0040	0.0005	+0.104 * E-07	0.0040	0.2560	-0.372 * E-02
0.0080	0.0005	+0.150 * E-08	0.0080	0.2560	-0.369 * E-02
0.0160	0.0005	+0.114 * E-07	0.0160	0.2560	-0.364 * E-02
0.0320	0.0005	-0.870 * E-09	0.0320	0.2560	-0.355 * E-02
0.0640	0.0005	-0.690 * E-08	0.0640	0.2560	-0.339 * E-02
0.1280	0.0005	+0.789 * E-09	0.1280	0.2560	-0.310 * E-02
0.2560	0.0005	-0.555 * E-08	0.2560	0.2560	-0.268 * E-02
0.5120	0.0005	-0.133 * E-08	0.5120	0.2560	-0.202 * E-02





(at constant methanol concentration) the concentration of acetone and the inconsistency parameter, and the trend here is a decrease in the inconsistency with increasing acetone concentration. These results seemed to prove that our hypothesis about the mechanism that triggered the oscillations in the convergence criterion was correct. We could add to that, however, that it is not the low concentrations of acetone in the system 'per se' that is the cause of erroneous predictions, but rather the low concentrations of acetone when accompanied by relatively large concentrations of methanol. To avoid further lack of convergence, the concentration of acetone in the last two stages (reboiler and one above) was set equal to zero. In no case previously had any of these concentrations been larger than 5%, so that the errors involved in this approximation should be acceptable.

#### 9.4 Optimization of the Acetone-Methanol-Water Tower

The effect of variations in the solvent feed rate and the reflux ratio on the performance of the column was studied with this system also. The column used contained 25 ideal stages, with the solvent feed being introduced in stage 8 and the process feed in stage 20. This configuration was chosen for the closeness of the acetone concentration in D to that of the actual column. Figure 9.3 shows the dependence of percent methanol recovery on the reflux ratio at



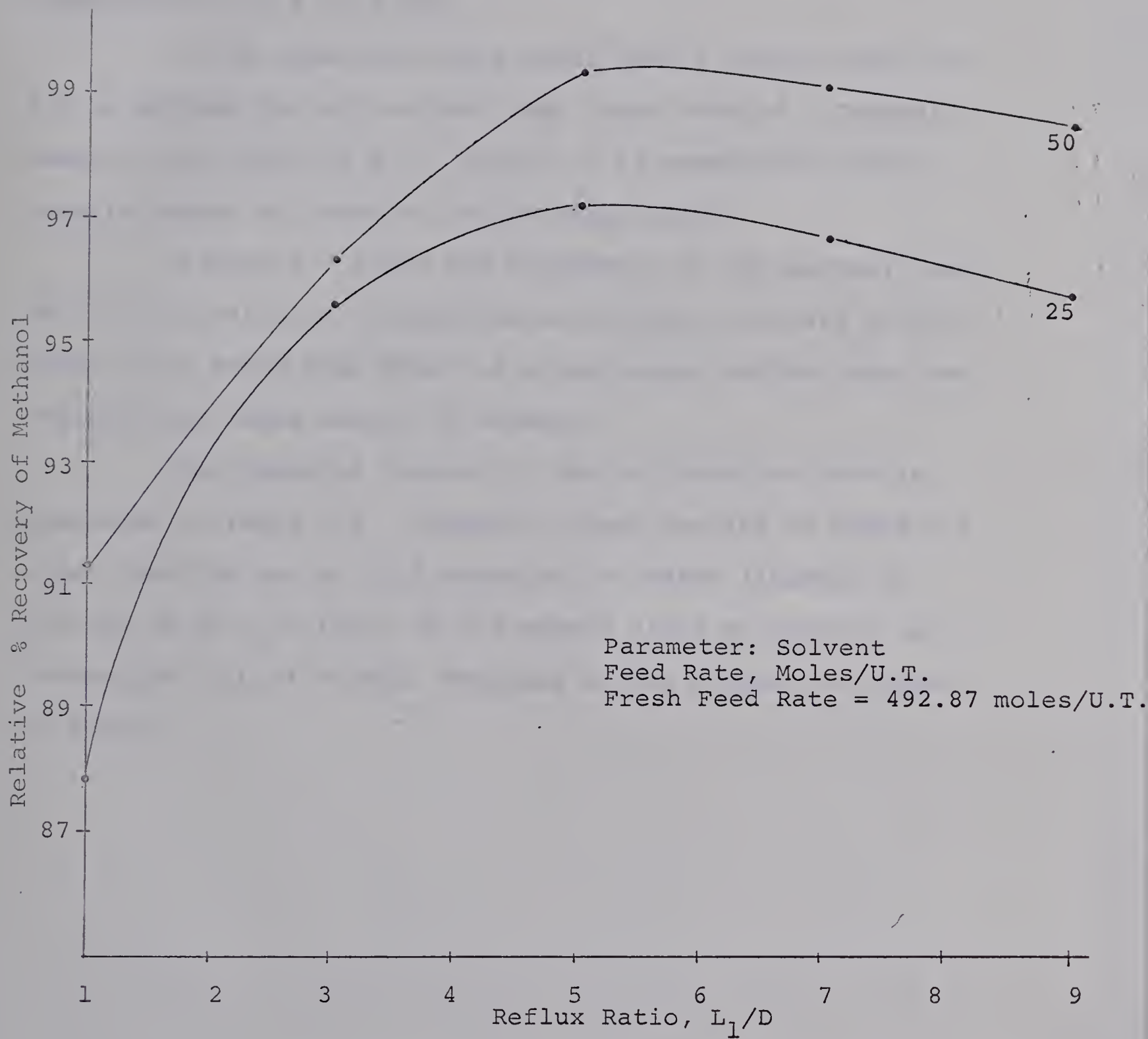


Figure 9.3 Variation of Methanol Recovery with Reflux Ratio



different solvent feed rates. The recovery of methanol figures are only relative due to the setting of the acetone concentration in B to 0.000.

It is clear from this curve that a reflux ratio of 5.0 is optimum for all solvent feed rates studied. Chemcell uses an  $L_1/D$  ratio of 4.13, though it is understood that a certain amount of internal reflux takes place.

Figure 9.4 shows the dependence of the solvent feed rate on  $L/D$  ratio at the particular methanol recovery of 97%. Again it is shown that there is a particular reflux rate that requires the least amount of solvent.

The detailed results of the optimization work is presented in Table 9.5. Comparing these results to Table 9.1 shows that the use of 50.0 moles/hr. of water (instead of 115.56) at an  $L_1/D$  ratio of 5.0 should yield an acetone concentration in D of 0.9522, compared to the industrial values of 0.957.





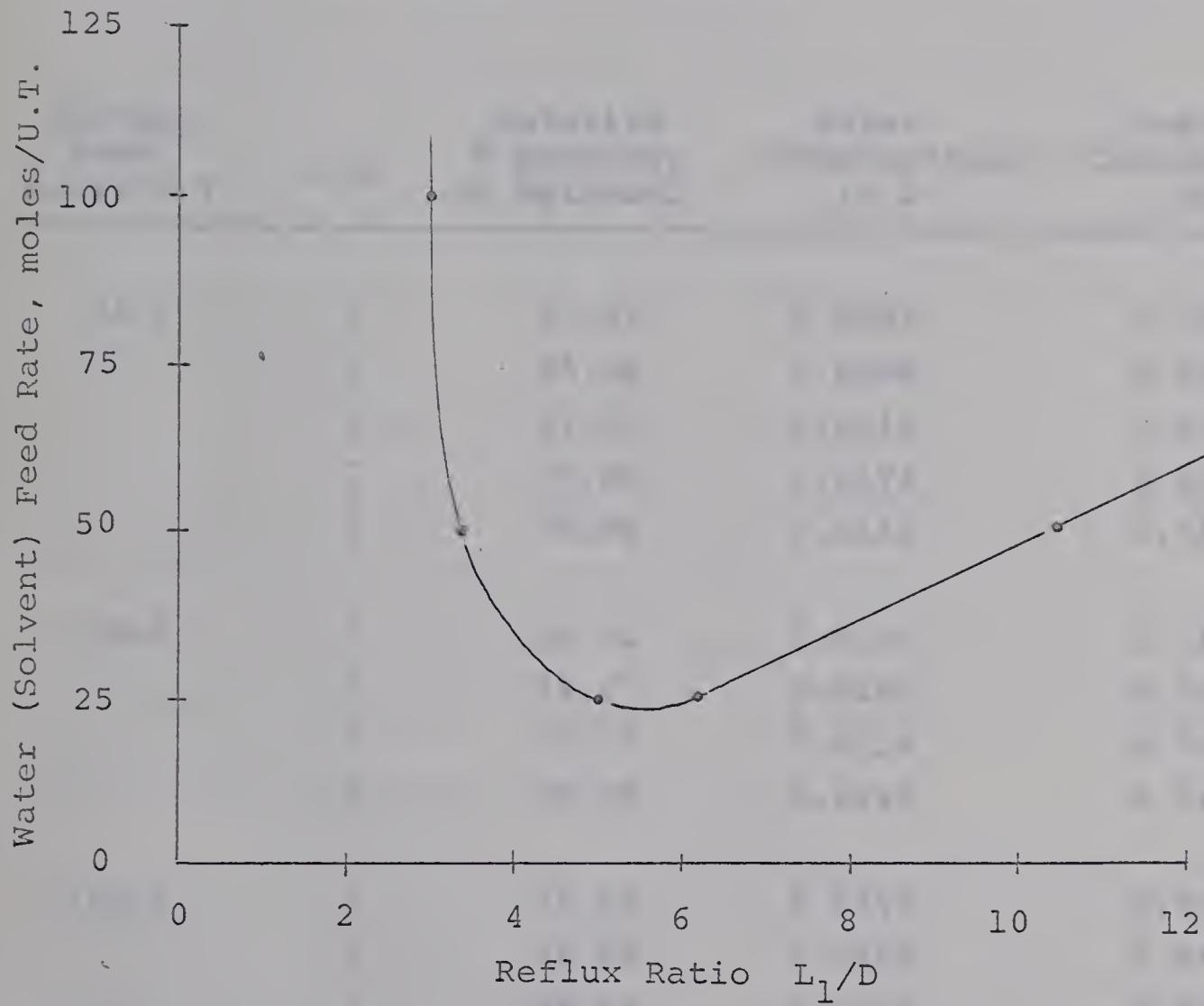


Figure 9.4 Variation of Solvent Feed Rate with Reflux Ratio % Methanol Recovery = 97



Table 9.5

Optimization of System Acetone-Methanol-Water

Total no. of plates	=	25
Solvent feed location	=	8
Fresh feed location	=	20
Fresh feed rate	=	492.87 moles/U.T.
Water concentration in D	≤	0.100

Solvent Feed moles/U.T.	$L_1/D$	Relative % Recovery of Methanol	Water Concentration in D	Acetone Concentration in D
25.0	1	87.99	0.0901	0.7040
	3	95.64	0.0206	0.9021
	5	97.27	0.0210	0.9264
	7	96.68	0.0174	0.9208
	9	95.88	0.0143	0.9115
50.0	3	96.32	0.0235	0.9100
	5	99.43	0.0285	0.9522
	7	99.12	0.0254	0.9506
	9	98.59	0.0226	0.9453
100.0	3	96.09	0.0243	0.9071
	5	98.98	0.0282	0.9479
	7	99.49	0.0279	0.9559
	9	100.0	0.0286	0.9645





## X. DISCUSSION OF RESULTS

### 10.1 Equilibrium Data Sources

Several correlations providing vapor-liquid equilibrium data have been used during this work. Problems I and II used a polynomial correlation. The main goal with those problems was to check the soundness of the developed programs by comparing the solutions to published information. Both problems duplicated the results of Wang and Henke<sup>26</sup>, problem I converging in 4 rather than the reported 7 iterations due to our normalization of the liquid composition at the end of every iteration.

The only difference between problems II and III is that while problem II uses polynomial data, problem III studies the same problem using Chao-Seader<sup>3</sup> equilibrium data. It can be seen from the results in Appendix III that temperature differences higher than 6°F on some stages can be caused by the use of the different data sources.

A relatively new equilibrium correlation is that proposed by Orye and Prausnitz<sup>4</sup>. In this model, the liquid phase activity coefficients are calculated by the Wilson equation<sup>14</sup>. This model was used in problems V and VI. The systems treated in those problems were common enough that no difficulty was encountered in finding binary equilibrium data for them. At least one point in every binary is necessary in



the determination of the Wilson or the interaction energy parameters which are then used in the prediction of the liquid phase activity coefficients.

## 10.2 Discussion of the Wilson Model

Although only one equilibrium point in every binary is necessary for the determination of the interaction energy parameters, it can be seen from Table 6.1 that the values of the interaction energy parameters and consequently their ability to predict activity coefficients vary with the composition point at which they are determined. This necessitated their optimization to determine the pair of interaction energies which, when used with the Prausnitz model<sup>4</sup>, predicted the equilibrium data with the minimum standard deviation.

The Wilson model<sup>14</sup> for the calculation of liquid phase activity coefficients offers two outstanding advantages over other methods:

- 1) The liquid phase activity coefficients in a multicomponent system can be calculated from parameters obtained from the binary equilibria in the system. This is an important advantage since binary equilibrium data are more readily available than multicomponent data.
- 2) As has been shown in Chapter VI, the interaction energy parameters are independent of temperature, i.e., once the optimum interaction energies have been calculated for





a system under particular conditions, they can be used to calculate liquid activity coefficients for the same system under removed temperature conditions. This is a strong point in favor of the Wilson model. It makes the model particularly useful in the design of isobaric distillation columns where large temperature variations occur in the column.

The relative independence of the interaction energies from temperature has been well demonstrated in Table 6.4 where optimum interaction energies obtained from isobaric binaries at 100°C predicted, using the Prausnitz model, the vapor-liquid equilibria of the same binaries at temperatures ranging from 58.2 to 70.0°C.

### 10.3 Relative Timings of the Equilibrium Models

Table 10.1 shows the relative timing for the equilibrium ratio correlations used in this work. From this table, it is evident that the time required increases with the complexity of the correlation used. The table shows that it takes roughly three times as long to use the Chao-Seader correlation as it does to use polynomial equilibrium ratios. The Prausnitz correlation using the Wilson model takes roughly four times as long as the polynomial.





Table 10.1

Relative Timings for the Different

Equilibrium Ratio Correlations

Problem Number	Equilibrium Correlation Used	Enthalpy Correlation Used	Timing on 7040 secs/iteration/component/stage	Number of Iterations
1	Polynomial in Temperature	Polynomial in Temperature	0.040	4
2	Polynomial in Temperature	Polynomial in Temperature	0.036	10
3	Chao-Seader	Chao-Seader	0.084	7
4	Chao-Seader	Chao-Seader	0.120	10
5	Prausnitz Model Using liquid activity coefficients from the Wilson model	Linear with heat of solution adjustments	0.157	34

The following unspecified routines are common among the problems  
 Tri-diagonal matrix solution for  $x_{ij}$   
 Muller's method for  $T_j$   
 Conventional enthalpy balances



#### 10.4 Comparison of Enthalpy Data Sources

Other than the polynomial fit, the two main sources of enthalpy data in this work have been the Chao-Seader<sup>3</sup> model and ideal enthalpies with adjustments made for heats of solution. The advantage of the Chao-Seader model over other semi-empirical data sources is the fact that the parameters calculated in the process of determining equilibrium ratios can also be used to calculate enthalpy departures for the same components.

The second method of enthalpy data calculations has been used with the two extractive distillation problems V and VI. The two methods for the calculation of heats of solution were presented in Section 5.7. The second method, which avoids the use of the Pierotti correlation, was used exclusively in this work. As will be shown later, the success of the simulation work done with the acetone-methanol-water system in problem VI shows that the enthalpy data used were adequate.

#### 10.5 Method of Solution and Convergence

The method exclusively used in this work to solve the material balance equations and determine the component distribution in the column was the tridiagonal matrix method coupled with a Gauss elimination algorithm<sup>26</sup>. The method is numerically stable and the subtraction of nearly equal quanti-







ties is avoided. Also, no matrix inversion operations are necessary which was the disadvantage of the matrix method presented by Amundson<sup>23</sup>. Muller's method for the determination of bubble point temperatures was also exclusive to all other methods. In most cases convergence occurred in the second iteration. The use of the Muller method has been computed by others<sup>28</sup> to cut solution times by at least a factor of three over the Erbar technique.

Problem IV used both of these algorithms to study a stabilizer problem which has already been studied using the Thiele-Geddes method<sup>39</sup> for the solution of the material balance equations. The computation time for the tridiagonal and Muller algorithms was 5 minutes and 29 seconds, as compared to 3 minutes and 55 seconds for the Thiele-Geddes method. These timings, however, are not strictly comparable since the initial assumptions used by Tatuch<sup>39</sup> were not reported. Our initial assumptions and results are reported in Appendix III.

The distinct advantage of the tridiagonal matrix solution is the ease with which it can handle additional feeds and sidestreams. The solution model makes provisions for a feed stream, a liquid and vapor sidestreams and a heat exchange device in every stage.



## 10.6 Possibility of Column Simulation and Optimization

The results of the simulation of an industrial column were presented in Chapter IX. The system was an acetone-methanol mixture being extractively distilled with water and the top product was acetone. The information supplied by Chemcell Ltd. was reported in Figure 9.1 and Table 9.1. This information can be summarized as follows:

- Composition of feed and product streams.
- Flow rates and temperatures of the feed and product streams.
- Temperatures at a number of points in the column.

This information allowed the assumption of initial vapor, liquid, and temperature profiles. The following step in the simulation was to duplicate the product compositions by varying the number of stages and/or the feed plate locations. The same reflux ratio and feed rates as in the industrial column were used.

Once the product compositions were duplicated, the optimization of the reflux ratio and the ratio of the feeds required the holding of the total number of plates and the feed locations constant. This is tantamount to assuming constant plate efficiencies regardless of the magnitudes of the operating variables, which limits the value of the optimization. Accordingly, if the optimum values of the operating variables are widely different from their values in the





simulated column, a new simulation should be attempted.

A comparison of some of the simulated and industrial temperatures is shown below:

	<u>Simulation</u>	<u>Industrial</u>
Condenser input ( $V_2$ )	133.24 $^{\circ}$ F	135.5 $^{\circ}$ F
Bottoms product	194.3 $^{\circ}$ F	approx. 194 $^{\circ}$ F

The closeness of the simulated and the industrial temperatures, shows that the method of calculating component enthalpies by adjusting ideal enthalpies with heats of mixing is quite adequate.

A comparison of the optimization work reported in Figures 8.4 and 9.4 shows that the optimum operating conditions in the phenol-MCH-toluene system occur in a much smaller range of reflux ratio than in the acetone-methanol-water system. Thus, the optima in the MCH-toluene system might be considered only local optima valid for that short range of reflux ratios only, and that some higher combination of reflux and feed ratios might be a universal optimum. Although this is possible, the reflux ratios in this system were investigated up to  $L_1/D$  values of 30.0 without such a combination occurring, and it is doubtful whether higher values of  $L_1/D$  would be of any practical interest.





## XI - SUGGESTIONS FOR FUTURE WORK

Future work in this field should proceed the following directions:

1. The development of an equilibrium model where the parameters used can be derived from intrinsic properties of the components in the system. In the Wilson model  $\lambda_{ij}$  and  $\lambda_{ii}$  are only 'proportional' to the i-j and i-i interaction energies respectively, and the interaction energy parameter ( $\lambda_{ij} - \lambda_{ii}$ ) cannot be rigorously defined<sup>4,10</sup>, so that the main concept is not based on any fundamental properties of the components i and j. The development of a model where this is the case would have wide applications in chemical engineering in general and extractive distillation in particular.
2. Investigate the possibility of using the parameter ( $\lambda_{ij} - \lambda_{ii}$ ) to determine the best solvent for the extractive distillation of a system. Since we know that:
  - a) The action of a solvent is to reduce the inter-molecular bonds in a system thus leading to more mobility and a higher volatility, and that



- b) the 1-2 interaction energy increases as stronger molecular and hydrogen bonds exist in a binary<sup>4,10</sup>.

It should then be possible to predict solvent action a priori by deciding on the relative magnitudes of the 1-2 interaction energies between the solvent and the light-key component and between the solvent and the heavy-key component. The wider the difference between these magnitudes, the more successful will be the solvent.

If this idea is feasible, and if the concept  $(\lambda_{ij} - \lambda_{ii})$  can be based on a more fundamental basis, choosing a solvent for extractive distillation would lose the element of art and experience in it and tend to be based on basic principles.

3. Develop a deeper insight into the predictive properties of the interaction energy parameters  $(\lambda_{ij} - \lambda_{ii})$ . Our work shows that widely different magnitudes of this parameter are able to predict vapor-liquid equilibria equally well. This could be due to any of two reasons or their combination:

- a) Minimum standard deviation, which is the parameter we have used to decide on the predictive ability of the interaction energies, is an insensitive indication of how well two vectors compare.







- b) Different magnitudes of the interaction energies, which cannot be a priori calculated, are inherently able to predict adequate equilibrium data.

The question then arises: Is it possible in a ternary system for example, to use two pairs of interaction energies at their optimum values and one grossly inaccurate pair and still predict good ternary vapor-liquid equilibria? If this is the case, then equilibrium data on each one of the binaries involved in multicomponent systems might not be necessary. This would be a milestone in equilibrium prediction with very limited data.

- 4. At the present stage, a tedious literature search is often necessary to locate data on the ideal enthalpies of the components being studied and the binary heats of solution at infinite dilution. The development of a generalized liquid enthalpy correlation that will take enthalpy departures due to heats of solution into account would be very helpful in extractive distillation design.



## DEFINITION OF SYMBOLS

A	constant in various expressions
AH	constant in enthalpy correlation of Chao-Seader
B	constant in various expressions second virial coefficient
BH	constant in enthalpy correlation of Chao-Seader
C	number of components
CH	constant in enthalpy correlation of Chao-Seader
DH	constant in enthalpy correlation of Chao-Seader
$f^o(p_o)$	reference fugacity: fugacity of the pure saturated component as a liquid at zero pressure
$g^E$	excess Gibbs energy of mixing
F	feed rate, moles/U.T.
f	the fugacity
H	enthalpy in the vapor phase, BTU/lb.mole
h	enthalpy in the liquid phase, BTU/lb.mole
K	vaporization constant
L	liquid flow rate, moles/U.T. partial molar heat of solution
N	number of stages
NCP	number of components
$P^S$	saturation vapor pressure
Q	heat load, BTU/U.T.
U	liquid sidestream flow rate, moles/U.T.
V	vapor flow rate, moles/U.T.
$v^L$	molar liquid volume, $\text{cm}^3/\text{mole}$



W	vapor sidestream flow rate, moles/U.T.
x	liquid composition, mole %
Y	vapor composition, mole %
Z	feed composition, mole %
	compressibility factor
$\gamma$	activity coefficient in liquid phase
$\phi^S$	fugacity coefficient at $p^S$
$\phi$	fugacity coefficient in vapor phase
$\lambda_{ij}$	proportional to interaction energy between i and j, cal/gm.mole
$\Lambda$	Wilson parameter
$\mu$	f/p ratio in liquid phase
$\omega$	acentric factor
$\delta$	solubility parameter.





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and  $\epsilon_{ij}$  is the interaction energy between the spins  $S_i$  and  $S_j$ .

The partition function is defined as

$$Z = \sum_{\{S_i\}} e^{-\beta H}$$

$$= \sum_{\{S_i\}} e^{-\beta \sum_i J_i S_i - \beta \sum_{\langle ij \rangle} \epsilon_{ij} S_i S_j} = \sum_{\{S_i\}} e^{-\beta \sum_i J_i S_i} \prod_{\langle ij \rangle} e^{-\beta \epsilon_{ij} S_i S_j}$$

$$= \sum_{\{S_i\}} e^{-\beta \sum_i J_i S_i} \prod_{\langle ij \rangle} \left( \sum_{S_i, S_j} e^{-\beta \epsilon_{ij} S_i S_j} \right) = \sum_{\{S_i\}} e^{-\beta \sum_i J_i S_i} \prod_{\langle ij \rangle} \left( \sum_{S_i, S_j} e^{-\beta \epsilon_{ij} S_i S_j} \right)$$

$$= \sum_{\{S_i\}} e^{-\beta \sum_i J_i S_i} \prod_{\langle ij \rangle} \left( \sum_{S_i, S_j} e^{-\beta \epsilon_{ij} S_i S_j} \right)$$

# APPENDIX I

## EQUATIONS FOR THE OPTIMIZATION OF THE INTERACTION ENERGIES IN THE WILSON MODEL



Optimization of Interaction Energies  
in the Wilson Model

$$y_1 = f(c_1 x_1 \gamma_1)$$

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right)$$

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}(1-x_1)) + (1-x_1) \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12}(1-x_1)} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + (1-x_1)} \right)$$

Therefore,

$$\gamma_1 = \frac{\exp(1-x_1) \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12}(1-x_1)} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + (1-x_1)} \right)}{x_1 + \Lambda_{12}(1-x_1)}$$

Since

$$\Lambda_{ij} = \frac{V_j}{V_i} e^{-((\lambda_{ij} - \lambda_{ii})/RT)}$$

and defining

$$\Lambda_{12} = \frac{V_2}{V_1} e^{-A/RT} \quad \text{and} \quad \Lambda_{21} = \frac{V_1}{V_2} e^{-B/RT}$$

where

$$A = (\lambda_{12} - \lambda_{11}) \quad \text{and} \quad B = (\lambda_{21} - \lambda_{22})$$

we obtain

$$\gamma_1 = S' e^{P'}$$





where

$$P' = (1-x_1) \left( \frac{1}{x_1 \alpha + (1-x_1)} - \frac{1}{x_1 + \beta} \right)$$

$$S' = \left( \frac{x_1 + (1-x_1)}{\alpha} \right)^{-1}$$

$$\alpha = \frac{V_1}{V_2} e^{A/RT} = \frac{1}{\Lambda_{12}}$$

$$\beta = (1-x_1) \frac{V_2}{V_1} e^{B/RT} = \frac{1-x_1}{\Lambda_{21}}$$

Accordingly

$$y_1 = c_1 x_1 S' e^{P'}$$

Obtaining the differentials in Section 6.2 proceeds then as follows:

$$\frac{\partial y_1}{\partial A} = c_1 x_1 \frac{\partial \gamma_1}{\partial A} \qquad \frac{\partial y_1}{\partial B} = c_1 x_1 \frac{\partial \gamma_1}{\partial B}$$

$$\frac{\partial \gamma_1}{\partial A} = \frac{\partial (S' e^{P'})}{\partial A} = S' e^{P'} \frac{\partial P'}{\partial A} + e^{P'} \frac{\partial S'}{\partial A}$$

$$\frac{\partial P'}{\partial A} = (1-x_1) \left( - \frac{x_1 \frac{\partial \alpha}{\partial A}}{(x_1 \alpha + (1-x_1))^2} \right)$$

$$= (1-x_1) \left( \frac{-x_1 \frac{\alpha}{RT}}{(x_1 \alpha + (1-x_1))^2} \right)$$



$$\begin{aligned}
\frac{\partial S'}{\partial A} &= \frac{\partial}{\partial A} \left( x_1 + \frac{1-x_1}{\alpha} \right)^{-1} \\
&= - \left( x_1 + \frac{1-x_1}{\alpha} \right)^{-2} \left( \frac{-(1-x_1)\alpha}{RT \alpha^2} \right) \\
&= + \left( \frac{1-x_1}{RT \alpha} \right) \left( x_1 + \frac{1-x_1}{\alpha} \right)^{-2} \\
&= \frac{\left( \frac{1-x_1}{RT} \right) \alpha^2}{(x_1 \alpha + (1-x_1))^2} \\
&= \frac{\alpha(1-x_1)}{RT(x_1 \alpha + (1-x_1))^2}
\end{aligned}$$

Accordingly

$$\begin{aligned}
\frac{\partial \gamma_1}{\partial A} &= S' e^{P'} (1-x_1) \left( \frac{-\frac{x_1 \alpha}{RT}}{(x_1 \alpha + (1-x_1))^2} \right) \\
&\quad + e^{P'} \frac{\alpha(1-x_1)}{RT(x_1 \alpha + (1-x_1))^2} \\
\frac{\partial \gamma_1}{\partial B} &= \frac{\partial (S' e^{P'})}{\partial B} = S' e^{P'} \frac{\partial P'}{\partial B} + e^{P'} \frac{\partial S'}{\partial B} \\
\frac{\partial P'}{\partial B} &= - \frac{\partial}{\partial B} \left( \frac{1-x_1}{x_1 + \beta} \right) = - \left( \frac{-(1-x_1)(1-x_1) \left( \frac{V_2}{V_1} \right) \frac{e^{BRT}}{RT}}{(x_1 + \beta)^2} \right) \\
&= \frac{(1-x_1) \beta}{RT(x_1 + \beta)^2}
\end{aligned}$$





$$\frac{\partial S'}{\partial B} = 0$$

Accordingly

$$\frac{\partial \gamma_1}{\partial B} = S' e^{P'} \left( \frac{(1-x_1) \beta}{RT (x_1 + \beta)^2} \right)$$

defining

$$\eta = (x_1 \alpha + (1-x_1))$$

$$\zeta = \frac{e^{P'} \alpha (1-x_1)}{RT \eta^2}$$

$$\theta = \frac{(1-x_1) \beta e^{P'}}{RT (x_1 + \beta)^2}$$

then

$$\begin{aligned} \frac{\partial y_1}{\partial A} &= c_1 x_1 \frac{\partial \gamma_1}{\partial A} \\ &= c_1 x_1 (S' e^{P'} (1-x_1) \left( \frac{-x_1 \alpha}{RT \eta^2} \right) + e^{P'} \frac{\alpha (1-x_1)}{RT \eta^2}) \\ &= c_1 x_1 (S' (-x_1) \zeta + \zeta) \\ &= c_1 x_1 \zeta (1-x_1 S') \end{aligned}$$

and

$$\begin{aligned} \frac{\partial y_1}{\partial B} &= c_1 x_1 \frac{\partial \gamma_1}{\partial B} \\ &= c_1 x_1 S' \theta \end{aligned}$$



APPENDIX II

COMPUTER PROGRAM AND OUTPUT FOR

OPTIMIZED INTERACTION ENERGIES



WILSON POLYST.MODEC

C  
C CALCULATION OF OPTIMUM BINARY INTERACTION ENERGIES  
C USING THE TECHNIQUE OF QUAZILINEARIZATION

C  
100 FORMAT(1X,I3)  
102 FORMAT(1X,21HINITIAL GUESS      A =,F10.4,8H      ,      R =,F10.4)  
103 FORMAT(1X,13HITERATION NO.,13,2X,2HA =,F10.4,8H      ,      R =,F10.4)  
104 FORMAT(1HL)  
101 FORMAT(1X,4F12.5)  
105 FORMAT(1X,64H      X OBS      Y OBS      Y CALC  
1      ABS ERROR)  
106 FORMAT(1H1)  
107 FORMAT(10A6,2F10.4)  
108 FORMAT(1X,6F12.5)  
109 FORMAT(1X,4F16.8)  
DIMENSION X1(99),Y1(99),C(99),P(99),V1(99),V2(99),ALPHA(99),T(99)  
DIMENSION ERROR(99)  
DIMENSION FMT(14)  
DIMENSION Q(99),R(99),YCALC(99)  
DIMENSION BETA(99),PDASH(99),SDASH(99),ETA(99),ZETA(99),THETA(99)  
DIMENSION TDEGC(99)  
C  
C NSETS IS NO. OF SYSTEMS  
C FMT IS NAME OF SYSTEM  
C FMW IS MOL WT. OF COMPONENT 1  
C SMW IS MOL WT. OF COMPONENT 2  
C N IS NO. OF DATA POINTS IN THE SYSTEM  
C RHO, ALPHA, AND BETA ARE CONSTANTS IN THE DENSITY  
C EQUATIONS OF THE RESPECTIVE COMPONENTS  
C A AND R ARE THE INITIAL GUESSES  
C Y, X, C, AND T ARE THE DATA POINTS WHERE C IS GAMMA  
C M IS A COUNTER  
C AS FAR AS POSSIBLE, THE SYMBOLS USED ARE THE SAME AS  
C IN THE EQUATIONS THEY REPRESENT IN THE PREVIOUS APPENDIX  
C  
READ(5,100)NSETS  
DO 30 K=1,NSETS  
READ(5,107)(FMT(J),J=1,10),FMW,SMW  
READ(5,100)N  
READ(5,108)RHO1,ALPHA1,BETA1,RHO2,ALPHA2,BETA2  
READ(5,101)A,R  
346 DO 10 I=1,N  
READ(5,101)Y1(I),X1(I),C(I),T(I)  
10 CONTINUE  
347 WRITE(6,104)  
WRITE(6,107)(FMT(J),J=1,10)  
WRITE(6,102)A,R  
M=0  
WRITE(6,105)  
RR=1.987  
DO 96 I=1,N  
C(I)=(Y1(I)/X1(I))/C(I)  
TDEGC(I)=T(I)  
T(I)=273.16+T(I)  
V1(I)=FMW/(RHO1+ALPHA1\*TDEGC(I)\*0.001+0.000001\*BETA1\*TDEGC(I)\*\*2)  
V2(I)=SMW/(RHO2+ALPHA2\*TDEGC(I)\*0.001+0.000001\*BETA2\*TDEGC(I)\*\*2)  
ALPHA(I)=(V1(I)/V2(I))\*EXP(A/(RR\*T(I)))  
BETA(I)=(1.0-X1(I))\*(V2(I)/V1(I))\*EXP(R/(RR\*T(I)))  
ETA(I)=X1(I)\*ALPHA(I)+(1.0-X1(I))





```

PDASH(I)=(1.0-X1(I))*(1.0/ETA(I)-1.0/(X1(I)+BETA(I)))
SDASH(I)=ALPHA(I)/ETA(I)
YCALC(I)=C(I)*X1(I)*SDASH(I)*EXP(PDASH(I))
ERROR(I)=ABS(YCALC(I)-Y1(I))
WRITE(6,100)X1(I),Y1(I),YCALC(I),ERROR(I)
96 CONTINUE
WRITE(6,104)
11 SIGQSQ=0.0
SIGPR=0.0
SIGPY1=0.0
SIGPSQ=0.0
SIGQR=0.0
SIGQY1=0.0
SIGPQ=0.0
DO 12 I=1,N
ALPHA(I)=(V1(I)/V2(I))*EXP(A/(RR*T(I)))
BETA(I)=(1.0-X1(I))*(V2(I)/V1(I))*EXP(B/(RR*T(I)))
ETA(I)=X1(I)*ALPHA(I)+(1.0-X1(I))
PDASH(I)=(1.0-X1(I))*(1.0/ETA(I)-1.0/(X1(I)+BETA(I)))
SDASH(I)=ALPHA(I)/ETA(I)
YCALC(I)=C(I)*X1(I)*SDASH(I)*EXP(PDASH(I))
ZETA(I)=EXP(PDASH(I))*ALPHA(I)*(1.0-X1(I))/(RR*T(I)*ETA(I)**2)
THETA(I)=(1.0-X1(I))*BETA(I)*EXP(PDASH(I))/(RR*T(I)*(X1(I)+BETA(I)
1**2))
P(I)=C(I)*X1(I)*ZETA(I)*(1.0-X1(I)*SDASH(I))
Q(I)=C(I)*X1(I)*SDASH(I)*THETA(I)
R(I)=YCALC(I)-A*P(I)-P*Q(I)
SIGQSQ=SIGQSQ+Q(I)**2
SIGPR=SIGPR+P(I)*R(I)
SIGPY1=SIGPY1+P(I)*Y1(I)
SIGPSQ=SIGPSQ+P(I)**2
SIGQR=SIGQR+Q(I)*R(I)
SIGQY1=SIGQY1+Q(I)*Y1(I)
SIGPQ=SIGPQ+P(I)*Q(I)
12 CONTINUE
R1=(SIGPSQ*SIGQR-SIGPSQ*SIGQY1+SIGPQ*SIGPY1-SIGPQ*SIGPR)/(SIGPQ**2
1-SIGPSQ*SIGQSQ)
A1=(SIGPY1-R1*SIGPQ-SIGPR)/SIGPSQ
M=M+1
WRITE(6,103)M,A1,R1
IF(ABS(A1-A).LE.1.0E-03)GO TO 16
A=A1
R=R1
GO TO 11
16 IF(ABS(R1-R).LE.1.0E-03)GO TO 15
A=A1
R=R1
GO TO 11
15 WRITE(6,104)
WRITE(6,105)
40 DO 20 I=1,N
ERROR(I)=ABS(YCALC(I)-Y1(I))
WRITE(6,109)X1(I),Y1(I),YCALC(I),ERROR(I)
20 CONTINUE
WRITE(6,106)
30 CONTINUE
END

```



# ACETONE-WATER SYSTEM

INITIAL GUESS      A = 466.0000      ,      B = 1653.0000

ITERATION NO.	1	A =	545.1388	,	B =	1595.2224
ITERATION NO.	2	A =	566.4876	,	B =	1582.7030
ITERATION NO.	3	A =	569.6239	,	B =	1579.8546
ITERATION NO.	4	A =	570.4456	,	B =	1579.1616
ITERATION NO.	5	A =	570.6365	,	B =	1578.9937
ITERATION NO.	6	A =	570.6831	,	B =	1578.9529
ITERATION NO.	7	A =	570.6947	,	B =	1578.9429
ITERATION NO.	8	A =	570.6973	,	B =	1578.9406
ITERATION NO.	9	A =	570.6981	,	B =	1578.9400

X OBS	Y OBS	Y CALC	ABS ERROR
0.10000000	0.76000000	0.78132080	0.02132080
0.20000000	0.79000000	0.74836183	0.04163817
0.30000000	0.81500000	0.76713257	0.04786743
0.40000000	0.83000000	0.82070781	0.00929219
0.50000000	0.84000000	0.83688446	0.00311554
0.60000000	0.86000000	0.91405127	0.05405127
0.70000000	0.87000000	0.91921479	0.04921479
0.80000000	0.90000000	0.91942493	0.01942493
0.90000000	0.94000000	0.93908454	0.00091545







# ACETONE-METHANOL SYSTEM

INITIAL GUESS      A = -220.9000      ,      B = 596.0000

ITERATION NO.	1	A = -250.7115	,	B = 608.2608
ITERATION NO.	2	A = -249.7374	,	B = 610.7667
ITERATION NO.	3	A = -250.2654	,	B = 611.6919
ITERATION NO.	4	A = -250.3610	,	B = 611.9687
ITERATION NO.	5	A = -250.3965	,	B = 612.0561
ITERATION NO.	6	A = -250.4070	,	B = 612.0833
ITERATION NO.	7	A = -250.4116	,	B = 612.0926
ITERATION NO.	8	A = -250.4127	,	B = 612.0954
ITERATION NO.	9	A = -250.4130	,	B = 612.0963

X OBS	Y OBS	Y CALC	ABS ERROR
0.10000000	0.18000000	0.19743172	0.01743172
0.20000000	0.30000000	0.29693533	0.00306467
0.30000000	0.42000000	0.41453840	0.00546160
0.40000000	0.51000000	0.49012692	0.01987308
0.50000000	0.60000000	0.58743420	0.01256580
0.60000000	0.67500000	0.69760516	0.02260516
0.70000000	0.73000000	0.74952030	0.01952031
0.80000000	0.80000000	0.80860055	0.00860056
0.90000000	0.89000000	0.91286954	0.02286953



APPENDIX III

PROBLEM STATEMENTS, INITIAL AND FINAL PROFILES,  
AND PRODUCT COMPOSITIONS  
FOR PROBLEMS I TO IV INCLUSIVE



PROBLEM NO. 1  
ONE-FEED FRACTIONATOR  
PROBLEM STATEMENT AND DATA

A. COLUMN DATA

PRESSURE= 250.0 PSIG

NO. OF PLATES= 16

CONDENSER TYPE= PARTIAL

OVERHEAD PRODUCT= 22.6 MOL VAPOR/U.T.

BOTTOM PRODUCT= 77.4 MOL/U.T.

REFLUX RATE= 154.3 MOL/U.T.

FEED PLATE NO.= 8

B. FEED DATA

TEMPERATURE= 225 F

RATE= 100 MOL/U.T.

VAPOR CONTENT= 16.4 MOL/100 MOL

COMPOSITION IN MOLE FRACTION

COMPONENT	COMPOSITION
-----------	-------------

C2	0.03
----	------

C3	0.20
----	------

C4	0.37
----	------

C5	0.35
----	------

C6	0.05
----	------

C. EQUILIBRIUM AND ENTHALPY DATA ARE POLYNOMIAL TEMPERATURE  
FUNCTIONS REPORTED BY---

AMUNDSON, N.R., AND PONTINEN, A.J., IND. ENG. CHEM., 50,  
730, (1958)





# PROBLEM NO. 1

## INITIAL PROFILE

STAGE	TEMP F	VAPCUR RATE MOLES/U.T.	LIQUID RATE MOLES/U.T.
1	110.000	0.2260000E 02	0.1543000E 03
2	123.000	0.1769000E 03	0.1543000E 03
3	136.000	0.1769000E 03	0.1543000E 03
4	149.000	0.1769000E 03	0.1543000E 03
5	162.000	0.1769000E 03	0.1543000E 03
6	175.000	0.1769000E 03	0.1543000E 03
7	188.000	0.1769000E 03	0.1543000E 03
8	201.000	0.1769000E 03	0.2379000E 03
9	214.000	0.1605000E 03	0.2379000E 03
10	227.000	0.1605000E 03	0.2379000E 03
11	240.000	0.1605000E 03	0.2379000E 03
12	253.000	0.1605000E 03	0.2379000E 03
13	266.000	0.1605000E 03	0.2379000E 03
14	279.000	0.1605000E 03	0.2379000E 03
15	292.000	0.1605000E 03	0.2379000E 03
16	305.000	0.1605000E 03	0.7740000E 02

## FINAL PROFILE

STAGE	TEMP F	VAPCUR RATE MOLES/U.T.	LIQUID RATE MOLES/U.T.
1	118.921	0.2260000E 02	0.1543000E 03
2	129.953	0.1769000E 03	0.1572289E 03
3	137.802	0.1798289E 03	0.1548853E 03
4	146.565	0.1774853E 03	0.1495772E 03
5	157.638	0.1721772E 03	0.1424170E 03
6	171.470	0.1650170E 03	0.1336754E 03
7	188.842	0.1562754E 03	0.1232551E 03
8	211.049	0.1458552E 03	0.2077797E 03
9	218.629	0.1303797E 03	0.2113498E 03
10	225.597	0.1339498E 03	0.2139129E 03
11	232.279	0.1365129E 03	0.2163277E 03
12	238.656	0.1389277E 03	0.2185323E 03
13	244.926	0.1411323E 03	0.2199648E 03
14	251.880	0.1425648E 03	0.2197723E 03
15	261.242	0.1423723E 03	0.2171495E 03
16	275.803	0.1397495E 03	0.7740000E 02

SUM (DELTA T\*\*2) AT ITERATION 4 = 0.068



## PRODUCT STREAM COMPOSITIONS

COMPONENT	CONDENSER STREAM	BOTTOM STREAM
C <sub>2</sub>	0.5048424E-01	0.1961257E-06
C <sub>3</sub>	0.9136172E 00	0.1001785E-01
C <sub>4</sub>	0.3585119E-01	0.4735912E 00
C <sub>5</sub>	0.4740653E-04	0.4518417E 00
C <sub>6</sub>	0.1407975E-07	0.6454911E-01





FINAL PROFILES AS REPORTED IN LITERATURE ( REF. 26 )

STAGE	TEMP F	VAPOUR RATE MOLES/U.T.	LIQUID RATE MOLES/U.T.
1	119.020	0.2260000E 02	0.1543000E 03
2	130.140	0.1769000E 03	0.1555400E 03
3	138.090	0.1781400E 03	0.1525400E 03
4	146.950	0.1751400E 03	0.1470500E 03
5	158.100	0.1696500E 03	0.1399200E 03
6	171.940	0.1625200E 03	0.1313000E 03
7	189.260	0.1539000E 03	0.1209000E 03
8	211.520	0.1435000E 03	0.2064100E 03
9	218.820	0.1290200E 03	0.2090600E 03
10	225.660	0.1316600E 03	0.2112900E 03
11	232.290	0.1338900E 03	0.2136100E 03
12	238.660	0.1362100E 03	0.2158300E 03
13	244.930	0.1384300E 03	0.2173400E 03
14	251.870	0.1399400E 03	0.2172500E 03
15	261.190	0.1398500E 03	0.2147600E 03
16	275.710	0.1373600E 03	0.7740000E 02



PROBLEM NO. 2  
TWO-FEED FRACTIONATOR  
PROBLEM STATEMENT AND DATA

A. COLUMN DATA

PRESSURE= 250.0 PSIG  
NO. OF PLATES= 21  
CONDENSER TYPE= PARTIAL  
FIRST FEED RATE= 34.5 MOL OF SATURATED VAPOR/U.T.  
FIRST FEED PLATE= 7  
SECOND FEED RATE= 65.5 MOL OF SATURATED LIQUID/U.T.  
SECOND FEED PLATE= 13  
FIRST SIDE STREAM= 15.0 MOL OF LIQUID/U.T.  
FIRST SIDESTREAM PLATE= 4  
SECOND SIDESTREAM= 25.0 MOL OF VAPOR/U.T.  
SECOND SIDESTREAM PLATE= 16  
OVERHEAD PRODUCT= 22.0 MOL VAPOR/U.T.  
REFLUX RATE= 71.806 MOL/U.T.

B. FEED DATA

FIRST FEED TEMPERATURE= 117.7 F  
SECOND FEED TEMPERATURE= 268.5 F

COMPONENT	FIRST FEED COMPOSITION MOLES/U.T.	SECOND FEED COMPOSITION MOLES/U.T.
METHANE	2.000	0.000
ETHANE	10.000	0.000
PROPYLENE	6.000	1.000
PROPANE	10.000	7.000
ISO-BUTANE	1.000	4.000
N-BUTANE	3.000	17.000
N-PENTANE	0.500	15.200
N-HEXANE	0.000	9.000
HEPTANE	0.000	4.500
OCTANE	0.000	4.300
OTHERS (360 F)	0.000	3.500
	-----	-----
	34.500	65.500

C. EQUILIBRIUM AND ENTHALPY DATA ARE POLYNOMIAL TEMPERATURE  
FUNCTIONS REPORTED BY ----

LYSTER, W.N., ET AL., PFT. REF., 38, NO. 6, 221, NO. 7,  
151, AND NO. 10, 139 (1959)





# INITIAL PROFILE

STAGE	TEMP F	VAPOUR RATE MOLES/U.T.	LIQUID RATE MOLES/U.T.
1	80.00	0.23000E 02	0.71810E 02
2	98.50	0.94810E 02	0.71810E 02
3	117.00	0.94810E 02	0.71810E 02
4	135.50	0.94810E 02	0.56810E 02
5	154.00	0.94810E 02	0.56810E 02
6	172.50	0.94810E 02	0.56810E 02
7	191.00	0.94810E 02	0.56810E 02
8	209.50	0.60310E 02	0.56810E 02
9	228.00	0.60310E 02	0.56810E 02
10	246.50	0.60310E 02	0.56810E 02
11	265.00	0.60310E 02	0.56810E 02
12	283.50	0.60310E 02	0.56810E 02
13	283.50	0.60310E 02	0.12231E 03
14	320.50	0.60310E 02	0.12231E 03
15	339.00	0.60310E 02	0.12231E 03
16	357.50	0.60310E 02	0.12231E 03
17	376.00	0.85310E 02	0.12231E 03
18	394.50	0.85310E 02	0.12231E 03
19	413.00	0.85310E 02	0.12231E 03
20	431.50	0.85310E 02	0.12231E 03
21	450.00	0.85310E 02	0.12231E 03

# FINAL PROFILE

STAGE	TEMP F	VAPOUR RATE MOLES/U.T.	LIQUID RATE MOLES/U.T.
1	77.38	0.23000E 02	0.71810E 02
2	94.87	0.94810E 02	0.72260E 02
3	103.69	0.95260E 02	0.71510E 02
4	111.11	0.94510E 02	0.54620E 02
5	120.75	0.92620E 02	0.52490E 02
6	131.14	0.90490E 02	0.50630E 02
7	141.21	0.88630E 02	0.48300E 02
8	169.09	0.51800E 02	0.49740E 02
9	185.99	0.53240E 02	0.50110E 02
10	198.05	0.53610E 02	0.49670E 02
11	208.71	0.53170E 02	0.47830E 02
12	222.68	0.51330E 02	0.42500E 02
13	253.29	0.46000E 02	0.10669E 03
14	257.65	0.44690E 02	0.10822E 03
15	262.79	0.46220E 02	0.10925E 03
16	269.56	0.47250E 02	0.11006E 03
17	279.20	0.73060E 02	0.11004E 03
18	283.97	0.73040E 02	0.10918E 03
19	294.58	0.72180E 02	0.10715E 03
20	311.34	0.70150E 02	0.10194E 03
21	344.73	0.64940E 02	0.37000E 02





# PRODUCT STREAM COMPOSITIONS

COMPONENT	CONDENSER RECYCLE	BOTTOM STREAM
ETHANE	0.0088	0.0000
ETHANE	0.2133	0.0000
PROPYLENE	0.2264	0.0000
PROPANE	0.5264	0.0007
ISOBUTANE	0.0095	0.0172
N-BUTANE	0.0056	0.1421
N-PENTANE	0.0000	0.3063
N-HEXANE	0.0000	0.2131
HEPTANE	0.0000	0.1141
OCTANE	0.0000	0.1127
OTHERS (360 F)	0.0000	0.0939



FINAL PROFILES AND COMPOSITION AS REPORTED IN LITERATURE (REF. 26)

STAGE	TEMP F	VAPOUR RATE MOLES/U.T.
1	77.290	0.2300000E 02
2	94.770	0.9480600E 02
3	103.610	0.9534200E 02
4	111.070	0.9461700E 02
5	120.780	0.9271300E 02
6	131.270	0.9055700E 02
7	141.410	0.8869100E 02
8	169.450	0.5236900E 02
9	186.400	0.5386300E 02
10	198.520	0.5424200E 02
11	209.140	0.5382700E 02
12	222.910	0.5199700E 02
13	253.420	0.4659000E 02
14	257.560	0.4447900E 02
15	262.510	0.4580900E 02
16	269.050	0.4681400E 02
17	275.440	0.7265200E 02
18	282.950	0.72658000E 02
19	293.300	0.77180500E 02
20	309.880	0.76977500E 02
21	343.330	0.64589000E 02

COMPONENT	LIQUID SIDESTREAM	VAPOUR SIDESTREAM
METHANE	0.26010E-01	0.19480E-10
ETHANE	0.88760E 00	0.20810E-04
PROPYLENE	0.29773E 01	0.21480E 00
PROPANE	0.88691E 01	0.19773E 01
I-BUTANE	0.99410E 00	0.32555E 01
N-BUTANE	0.12404E 01	0.13705E 02
N-PENTANE	0.54800E-02	0.42934E 01
HEXANE	0.41940E-06	0.11099E 01
HEPTANE	0.34570E-09	0.28010E 00
OCTANE	0.24280E-12	0.13390E 00
OTHERS (360)	0.16310E-18	0.29660E-01





PROBLEM NO. 3  
TWO-FEED FRACTIONATOR  
PROBLEM STATEMENT AND DATA

A. COLUMN DATA

PRESSURE= 250.0 PSIG  
NO. OF PLATES= 21  
CONDENSER TYPE= PARTIAL  
FIRST FEED RATE= 34.5 MOL OF SATURATED VAPOR/U.T.  
FIRST FEED PLATE= 7  
SECOND FEED RATE= 65.5 MOL OF SATURATED LIQUID/U.T.  
SECOND FEED PLATE= 13  
FIRST SIDE STREAM= 15.0 MOL OF LIQUID/U.T.  
FIRST SIDESTREAM PLATE= 4  
SECOND SIDESTREAM= 25.0 MOL OF VAPOR/U.T.  
SECOND SIDESTREAM PLATE= 16  
OVERHEAD PRODUCT= 23.0 MOL VAPOR/U.T.  
REFLUX RATE= 71.806 MOL/U.T.

B. FEED DATA

FIRST FEED TEMPERATURE= 117.7 F  
SECOND FEED TEMPERATURE= 268.5 F

COMPONENT	FIRST FEED COMPOSITION MOLES/U.T.	SECOND FEED COMPOSITION MOLES/U.T.
METHANE	2.000	0.000
ETHANE	10.000	0.000
PROPYLENE	6.000	1.000
PROPANE	10.000	7.000
ISO-BUTANE	1.000	4.000
N-BUTANE	3.000	17.000
N-PENTANE	0.500	15.200
N-HEXANE	0.000	9.000
HEPTANE	0.000	4.500
OCTANE	0.000	4.300
OTHERS (360 F)	0.000	3.500
	-----	-----
	34.500	65.500

C. EQUILIBRIUM AND ENTHALPY DATA ARE CHAO-SEADER DATA  
THE CONSTANTS FOR WHICH ARE REPORTED IN THE NEXT PAGES



COMPONENT PHYSICAL PROPERTIES  
FOR CHAO SEADER CORRELATION

COMPONENTS	TC	PC	W	DELTA	V1
H2S	672.48	1306.5	0.0868	8.800	42.1
NITROGEN	227.16	492.2	0.0206	4.440	53.0
CO2	547.56	1071.3	0.1768	7.120	44.0
METHANE	343.90	673.1	0.0000	5.680	52.0
ETHYLENE	509.50	742.1	0.0940	6.080	61.0
ETHANE	550.50	709.8	0.1064	6.050	68.0
PROPYLENE	657.20	667.0	0.1451	6.430	79.0
PROPANE	665.90	617.4	0.1538	6.400	84.0
1-BUTENE	755.3	582.0	0.2085	6.760	95.2
I-BUTANE	734.70	529.1	0.1825	6.730	105.5
N-BUTANE	765.20	550.7	0.1953	6.730	101.4
I-PENTANE	829.8	483.0	0.2104	7.021	117.4
N-PENTANE	845.60	489.5	0.2387	7.021	116.1
N-HEXANE	914.20	440.0	0.2972	7.266	131.6
N-HEPTANE	972.30	396.8	0.3403	7.430	147.5
N-OCTANE	1024.90	362.1	0.3992	7.551	163.5
N-NONANE	1073.00	332.0	0.4439	7.649	179.6
N-DECANE	1114.00	304.0	0.4869	7.721	196.0

CHAO SEADER ENTHALPY CONSTANTS

COMPONENTS	AH	BH	CH	DH
H2S	0.3659210E 04	0.8033766E 01	0.6508904E-03	0.3250902E-06
NITROGEN	0.3192124E 04	0.6956438E 01	0.3103818E-04	0.2350028E-06
CO2	0.3357740E 04	0.8440110E 01	0.3040541E-02	-0.7897689E-06
METHANE	0.3683894E 04	0.7880800E 01	0.3505719E-02	0.2446472E-06
ETHYLENE	0.3791992E 04	0.9144806E 01	0.7819394E-02	-0.1522679E-05
ETHANE	0.4220126E 04	0.1120242E 02	0.8938123E-02	-0.8066164E-06
PROPYLENE	0.4714762E 04	0.1350214E 01	0.1146875E-01	-0.1797251E-05
PROPANE	0.5068633E 04	0.1510799E 02	0.1540639E-01	-0.2938696E-05
1-BUTENE	0.5934714E 04	0.1768871E 01	0.1763632E-01	-0.3901157E-05
I-BUTANE	0.6023067E 04	0.1999786E 02	0.2044134E-01	-0.4146112E-05
N-BUTANE	0.6654675E 04	0.2054464E 02	0.1865250E-01	-0.3016783E-05
I-PENTANE	0.7475643E 04	0.2465428E 02	0.2446248E-01	-0.4437345E-05
N-PENTANE	0.8039759E 04	0.2518989E 02	0.2348587E-01	-0.4174458E-05
N-HEXANE	0.9475028E 04	0.2952267E 02	0.2914070E-01	-0.5011897E-05
N-HEPTANE	0.1056589E 05	0.3331526E 02	0.3278746E-01	-0.6696126E-05
N-OCTANE	0.1226219E 05	0.3899065E 02	0.3841118E-01	-0.7945704E-05
N-NONANE	0.1366069E 05	0.4373618E 02	0.4301726E-01	-0.8954763E-05
N-DECANE	0.1505435E 05	0.4848591E 02	0.4756158E-01	-0.9858597E-05





CHAO-SEADER CONSTANTS FOR THE  
CALCULATION OF LIQUID FUGACITY COEFFICIENTS

GENERAL

METHANE

HYDROGEN

A( 1)	0.57574800E 01	0.24384000E 01	0.19671800E 01
A( 2)	-0.30176101E 01	-0.22455000E 01	0.10297200E 01
A( 3)	-0.49850000E 01	-0.34084000E 00	-0.54008900E-01
A( 4)	0.20229900E 01	0.21200000E-02	0.52880000E-03
A( 5)	0.	-0.22300000E-02	0.
A( 6)	0.84270000E-01	0.10486000E 00	0.85849999E-02
A( 7)	0.26667000E 00	-0.36910000E 01	0.
A( 8)	-0.31138000E 00	0.	0.
A( 9)	-0.26550000E-01	0.	0.
A(10)	0.28830000E-01	0.	0.
A(11)	-0.42389300E 01	0.	0.
A(12)	0.86580800E 01	0.	0.
A(13)	-0.12206000E 01	0.	0.
A(14)	-0.31522400E 01	0.	0.
A(15)	-0.25000000E-01	0.	0.
A(16)	0.	0.	0.

NITROGEN

CO2

H2S

A( 1)	0.27365534E 01	-0.30060874E 02	0.30581210E 01
A( 2)	-0.19818310E 01	0.61409853E 01	-0.26491906E 01
A( 3)	-0.51487289E 00	0.45263229E 02	0.37457945E 00
A( 4)	0.42470988E-01	-0.27303012E 02	-0.14647096E 01
A( 5)	-0.28143800E-02	0.59152545E 01	0.45734766E 00
A( 6)	-0.29474700E-01	0.36838431E 00	-0.95721679E 00
A( 7)	0.21495843E-01	-0.67916811E 00	0.14272648E 01
A( 8)	0.	0.15546365E 00	-0.50242238E 00
A( 9)	0.	0.	0.33950029E 00
A(10)	0.	0.89562849E-01	-0.26678483E 00
A(11)	0.	0.	0.
A(12)	0.	0.	0.
A(13)	0.	0.	0.
A(14)	0.	0.	0.
A(15)	0.	0.	0.
A(16)	0.	0.	0.





## PROBLEM NO. 3

## INITIAL PROFILE

STAGE	TEMP F	VAPCUR RATE MOLES/U.T.	LIQUID RATE MOLES/U.T.
1	80.000	0.2300000E 02	0.7180600E 02
2	101.500	0.9480600E 02	0.7180600E 02
3	111.000	0.9480600E 02	0.7180600E 02
4	118.500	0.9480600E 02	0.5680600E 02
5	126.000	0.9480600E 02	0.5680600E 02
6	135.500	0.9480600E 02	0.5680600E 02
7	143.000	0.9480600E 02	0.5680600E 02
8	150.500	0.6030600E 02	0.5680600E 02
9	174.000	0.6030600E 02	0.5680600E 02
10	189.500	0.6030600E 02	0.5680600E 02
11	201.000	0.6030600E 02	0.5680600E 02
12	215.500	0.6030600E 02	0.5680600E 02
13	247.000	0.6030600E 02	0.1223060E 03
14	251.500	0.6030600E 02	0.1223060E 03
15	257.000	0.6030600E 02	0.1223060E 03
16	264.500	0.6030600E 02	0.1223060E 03
17	272.000	0.8530600E 02	0.1223060E 03
18	280.500	0.8530600E 02	0.1223060E 03
19	292.000	0.8530600E 02	0.1223060E 03
20	311.500	0.8530600E 02	0.1223060E 03
21	349.000	0.8530600E 02	0.3700000E 02

## FINAL PROFILE

STAGE	TEMP F	VAPCUR RATE MOLES/U.T.	LIQUID RATE MOLES/U.T.
1	80.569	0.2300000E 02	0.7180600E 02
2	101.647	0.9480600E 02	0.7212441E 02
3	110.772	0.9512441E 02	0.7119993E 02
4	117.774	0.9419994E 02	0.5430282E 02
5	126.175	0.9230283E 02	0.5218358E 02
6	134.862	0.9018358E 02	0.5024468E 02
7	143.240	0.8824468E 02	0.4871027E 02
8	166.605	0.5221027E 02	0.4880472E 02
9	181.510	0.5230473E 02	0.4853166E 02
10	192.703	0.5203167E 02	0.4792088E 02
11	202.819	0.5142089E 02	0.4623972E 02
12	216.396	0.4973973E 02	0.4099080E 02
13	248.359	0.4449080E 02	0.1033959E 03
14	252.590	0.4139586E 02	0.1046293E 03
15	257.814	0.4262927E 02	0.1058483E 03
16	264.856	0.4384831E 02	0.1070336E 03
17	271.837	0.7003360E 02	0.1075631E 03
18	280.165	0.7056309E 02	0.1073619E 03
19	291.853	0.7036186E 02	0.1059080E 03
20	310.813	0.6890800E 02	0.1008616E 03
21	348.489	0.6386163E 02	0.3700000E 02

SUM (DELTA T\*\*2) AT ITERATION 7 = 0.840



# PRODUCT STREAM COMPOSITIONS

COMPONENT	CONDENSER RECYCLE	BOTTOM PRODUCT	LIQUID SIDESTREAM	VAPOUR SIDESTREAM
METHANE	0.1041E-01	0.2305E-15	0.2529E-02	0.7370E-10
ETHANE	0.2107E 00	0.2256E-09	0.6347E-01	0.1866E-05
PROPYLENE	0.2262E 00	0.6100E-04	0.1934E 00	0.9834E-02
PROPANE	0.5349E 00	0.9474E-03	0.5915E 00	0.8591E-01
I-BUTANE	0.1104E-01	0.1849E-01	0.6541E-01	0.1302E 00
N-BUTANE	0.6747E-02	0.1402E 00	0.8316E-01	0.5407E 00
N-PENTANE	0.3147E-05	0.3065E 00	0.4771E-03	0.1732E 00
N-HEXANE	0.1726E-10	0.2142E 00	0.3353E-07	0.4228E-01
HEPTANE	0.2139E-14	0.1140E	0.4105E-10	0.1095E-01
OCTANE	0.2753E-18	0.1122E 0	0.6351E-13	0.5538E-02
OTHERS (360)	0.2816E-25	0.9340E-01	0.5109E-18	0.1462E-02





FINAL PROFILES AND COMPOSITION AS REPORTED IN LITERATURE (REF. 26)

STAGE	TEMP F	VAPOUR RATE MOLES/U.T.
1	77.290	0.2300000E 02
2	94.770	0.9480600E 02
3	103.610	0.9534200E 02
4	111.070	0.9461700E 02
5	120.780	0.9271300E 02
6	131.270	0.9055700E 02
7	141.410	0.8869100E 02
8	169.450	0.5236900E 02
9	186.400	0.5386300E 02
10	198.520	0.5424200E 02
11	209.140	0.5382700E 02
12	222.910	0.5199700E 02
13	253.420	0.4659000E 02
14	257.560	0.4447900E 02
15	262.510	0.4580900E 02
16	269.050	0.4681400E 02
17	275.440	0.7265200E 02
18	282.950	0.72658000E 02
19	293.300	0.77180500E 02
20	309.880	0.76977500E 02
21	343.330	0.64589000E 02

COMPONENT	LIQUID SIDESTREAM	VAPOUR SIDESTREAM
METHANE	0.26010E-01	0.19480E-10
ETHANE	0.88760E 00	0.20810E-04
PROPYLENE	0.29773E 01	0.21480E 00
PROPANE	0.88691E 01	0.19773E 01
I-BUTANE	0.99410E 00	0.32555E 01
N-BUTANE	0.12404E 01	0.13705E 02
N-PENTANE	0.54800E-02	0.42934E 01
HEXANE	0.41940E-06	0.11099E 01
HEPTANE	0.34570E-09	0.28010E 00
OCTANE	0.24280E-12	0.13390E 00
OTHERS(360)	0.16310E-18	0.29660E-01



PROBLEM NO. 4  
STABILIZER PROBLEM  
PROBLEM STATEMENT AND DATA

A. COLUMN DATA

PRESSURE= 345.0 PSIA  
NO. OF PLATES= 17  
REFLUX RATIO= 3.1409  
DISTILLATE RATE= 0.44423 MOL/U.T.  
FEED PLATE NO.= 9

B. FEED DATA

FLASH TEMPERATURE= 321.83 F  
FEED LIQUID FRACTION= 0.5550  
FEED RATE= 1.00 MOL/U.T.

COMPOSITION IN MOLE FRACTION

COMPONENT	TOTAL FEED	FLASH LIQUID	FLASH VAPOUR
NITROGEN	0.5426E-03	0.81080E-04	0.11182E-02
H <sub>2</sub> S	0.1150E-00	0.49699E-01	0.19651E-00
CO <sub>2</sub>	0.1194E-01	0.33119E-02	0.22694E-01
METHANE	0.8410E-01	0.16673E-01	0.16820E-00
ETHANE	0.4069E-01	0.13322E-01	0.74834E-01
PROPANE	0.7379E-01	0.42770E-01	0.11248E-00
I-BUTANE	0.2930E-01	0.22792E-01	0.37416E-01
N-BUTANE	0.9333E-01	0.77259E-01	0.11336E-00
I-PENTANE	0.5209E-01	0.53857E-01	0.49883E-01
N-PENTANE	0.6131E-01	0.65553E-01	0.56023E-01
HEXANE	0.1145E-00	0.14675E-00	0.74246E-01
HEPTANE	0.1264E-01	0.18274E-00	0.56177E-01
OCTANE	0.6782E-01	0.10660E-00	0.19449E-01
NONANE	0.3961E-01	0.65587E-01	0.72082E-02
DECANE	0.8953E-01	0.15298E-00	0.10380E-01

C. EQUILIBRIUM AND ENTHALPY DATA ARE GIVEN BY THE CHAO-SEADER CORRELATION AND ARE REPORTED FOR PROBLEM 3



## PROBLEM NO. 4

## INITIAL PROFILE

STAGE	TEMP F	VAPOUR RATE MOLES/U.T.	LIQUID RATE MOLES/U.T.
1	140.000	0.4440000E 00	0.1390000E 01
2	170.000	0.1835000E 01	0.1390000E 01
3	190.000	0.1835000E 01	0.1390000E 01
4	210.000	0.1835000E 01	0.1390000E 01
5	230.000	0.1835000E 01	0.1390000E 01
6	250.000	0.1835000E 01	0.1390000E 01
7	270.000	0.1835000E 01	0.1390000E 01
8	270.000	0.1835000E 01	0.1390000E 01
9	290.000	0.1835000E 01	0.1945000E 01
10	330.000	0.1390000E 01	0.1945000E 01
11	350.000	0.1390000E 01	0.1945000E 01
12	370.000	0.1390000E 01	0.1945000E 01
13	390.000	0.1390000E 01	0.1945000E 01
14	410.000	0.1390000E 01	0.1945000E 01
15	430.000	0.1390000E 01	0.1945000E 01
16	450.000	0.1390000E 01	0.1945000E 01
17	470.000	0.1390000E 01	0.5550000E 00





# FINAL PROFILE

STAGE	TEMP F	VAPOUR RATE LBS/J.T.	LIQUID RATE LBS/J.T.
1	144.998	0.4442300E 00	0.1394800E 01
2	200.861	0.1839030E 01	0.1535460E 01
3	221.263	0.1979690E 01	0.1577217E 01
4	231.855	0.2021447E 01	0.1568736E 01
5	240.143	0.2012966E 01	0.1533695E 01
6	248.973	0.1977925E 01	0.1473319E 01
7	260.350	0.1917549E 01	0.1366142E 01
8	277.991	0.1810372E 01	0.1145798E 01
9	313.363	0.1590028E 01	0.1698264E 01
10	340.893	0.1142494E 01	0.1923782E 01
11	355.696	0.1368012E 01	0.2025938E 01
12	367.104	0.1470168E 01	0.2078199E 01
13	378.298	0.1522429E 01	0.2103306E 01
14	391.228	0.1547536E 01	0.2104910E 01
15	408.094	0.1549140E 01	0.2074433E 01
16	432.408	0.1518663E 01	0.2006643E 01
17	469.146	0.1450873E 01	0.5557700E 00

SUM (DELTA T\*\*2) AT ITERATION 17 = 0.938



# PRODUCT STREAM COMPOSITIONS

COMPONENT	CONDENSER STREAM	BOTTOM STREAM
NITROGEN	0.1226082E-02	0.1159296E-10
H <sub>2</sub> S	0.2601154E 00	0.5153156E-05
CO <sub>2</sub>	0.2699206E-01	0.4390543E-08
METHANE	0.1901034E 00	0.6825784E-08
ETHANE	0.9202315E-01	0.5990067E-07
PROPANE	0.1668011E 00	0.7923181E-04
I -BUTANE	0.6434291E-01	0.1534741E-02
N -BUTANE	0.1924372E 00	0.1481454E-01
I PENTANE	0.4459652E-02	0.8985036E-01
N-PENTANE	0.1526564E-02	0.1087113E 00
HEXANE	0.6031676E-05	0.2052455E 00
HEPTANE	0.3577392E-07	0.2266508E 00
OCTANE	0.8426215E-10	0.1215938E 00
NONANE	0.3024444E-12	0.7101077E-01
DECANE	0.5967158E-14	0.1605038E 00





## LITERATURE VALUES (REF. 39)

## THIELE GEDDES CALCULATION PROCEEDURE

BASIS ONE LB-MOLE FEED

COLUMN PRESSURE= 345.000 PSIA

DISTILLATE TEMP= 146.123

NO OF THEORETICAL PLATES= 16

REFLUX RATIO= 3.14091 DISTILLATE RATE= 0.44423 FEED PLATE NO= 8

STAGE	VAPOUR	LIQUID	TEMPERATURE
1	1.83951	1.53474	202.111
2	1.97897	1.57328	222.727
3	2.01751	1.56150	233.726
4	2.00573	1.52339	242.574
5	1.96762	1.45883	252.103
6	1.90306	1.34198	264.407
7	1.78621	1.65781	283.787
8	1.65704	1.90883	336.363
9	1.35306	2.02336	351.323
10	1.48759	2.08364	361.942
11	1.52787	2.11882	371.555
12	1.56305	2.13529	381.768
13	1.57952	2.13252	394.058
14	1.57675	2.09780	410.391
15	1.54203	2.02750	434.226
16	1.47173	0.55577	470.361

CONDENSER HEAT LOAD= 0.10755995E 05 BTU/LB MOLE FEED

REBOILER HEAT LOAD= 0.14896920E 05 BTU/LB MOLE FEED

## COMPOSITIONS IN MOLE FRACTIONS

COMPONENT	FEED	DISTILLATE	BOTTOMS
NITROGEN	0.54259359E-03	0.12214222E-02	0.20757247E-11
H2S	0.11502984E 00	0.25893895E 00	0.20417795E-05
CO2	0.11937059E-01	0.26871287E-01	0.11195078E-08
METHANE	0.84102007E-01	0.18932044E 00	0.14462437E-08
ETHANE	0.40694519E-01	0.91606643E-01	0.17935442E-07
PROPANE	0.73792728E-01	0.16605930E 00	0.43258454E-04
ISOBUTANE	0.29300054E-01	0.64459787E-01	0.11965750E-02
N-BUTANE	0.93326097E-01	0.19449211E 00	0.12463225E-01
ISOPENTANE	0.52088985E-01	0.51877448E-02	0.89577557E-01
N-PENTANE	0.61313076E-01	0.18341588E-02	0.10885509E 00
HEXANE	0.11448725E 00	0.81200844E-05	0.20599141E 00
HEPTANE	0.12642431E 00	0.53346457E-07	0.22747631E 00
OCTANE	0.57874196E-01	0.12479646E-09	0.12203667E 00
NONANE	0.39609332E-01	0.53066324E-12	0.71269417E-01
DECANE	0.89527942E-01	0.11019513E-13	0.16108841E 00



#### APPENDIX IV

PROBLEM STATEMENTS, INITIAL AND FINAL PROFILES,  
AND PRODUCT COMPOSITIONS FOR PROBLEMS V AND VI



PROBLEM NO. 5  
EXTRACTIVE DISTILLATION  
SYSTEM PHENOL-MCH-TOLUENE

A. COLUMN DATA

PRESSURE=ATMOSPHERIC  
NO. OF PLATES=21  
CONDENSER TYPE=TOTAL  
OVERHEAD PRODUCT=52.09 MOL/U.T.  
BOTTOM PRODUCT=247.91 MOL/U.T.  
REFLUX RATIO=5.0  
FEED PLATES= 5,14

B. FEED DATA

TEMPERATURE OF SOLVENT FEED=244.49 F  
RATE OF SOLVENT FEED= 200.0 MOL/U.T.  
TEMPERATURE OF FRESH FEED= 241.31 F  
RATE OF FRESH FEED= 100.0 MOL/U.T.

COMPONENT	COMPOSITION SOLVENT FEED	COMPOSITION FRESH FEED
PHENOL	0.9910	0.0000
MCH	0.0000	0.5000
TOLUENE	0.0090	0.5000

C. EQUILIBRIUM DATA ARE OBTAINED FROM THE SIMPLIFIED  
PRAUSNITZ MODEL USING WILSON'S EQUATION.

THE OPTIMIZED INTERACTION ENERGIES ARE IN CAL/GM.MOLE  
WHERE N=PHENOL M=MCH T=TOLUENE

INTERACTION ENERGY(N,L)= 155.2845  
INTERACTION ENERGY(L,N)= 953.399  
INTERACTION ENERGY(N,M)= 69.208  
INTERACTION ENERGY(M,N)= 1875.423  
INTERACTION ENERGY(M,L)= 238.507  
INTERACTION ENERGY(L,M)= - 32.162

D. ENTHALPY DATA ARE OBTAINED FROM IDEAL ENTHALPY  
FUNCTIONS WITH HEAT OF SOLUTION CORRECTIONS

THE INFINITE DILUTION HEATS OF SOLUTION ARE IN BTU/LB-MOL

HEAT OF DIL.(N,M) = HEAT OF DIL.(M,N)= 4520.0  
HEAT OF DIL.(N,L) = HEAT OF DIL.(L,N)= 2790.0  
HEAT OF DIL.(M,L) = HEAT OF DIL.(L,M)= 0.000  
THESE VALUES ARE OBTAINED FROM SMITH(6)





# INITIAL PROFILE

STAGE	TEMP F	VAPOUR RATE MOLES/U.T.	LIQUID RATE MOLES/U.T.
1	215.18	0.	0.26045F 03
2	215.54	0.31254F 03	0.25751F 03
3	216.42	0.30960F 03	0.25407F 03
4	220.50	0.30616F 03	0.24910F 03
5	240.14	0.30119F 03	0.42096F 03
6	240.51	0.32305F 03	0.41860F 03
7	240.89	0.32078F 03	0.41654F 03
8	241.26	0.31863F 03	0.41451F 03
9	241.62	0.31660F 03	0.41261F 03
10	241.96	0.31470F 03	0.41084F 03
11	242.26	0.31293F 03	0.40922F 03
12	242.42	0.31131F 03	0.40784F 03
13	241.89	0.30993F 03	0.40732F 03
14	237.32	0.30941F 03	0.50300F 03
15	237.56	0.30509F 03	0.50094F 03
16	238.08	0.30303F 03	0.49832F 03
17	238.64	0.30041F 03	0.49505F 03
18	239.43	0.29714F 03	0.49101F 03
19	240.80	0.29310F 03	0.48601F 03
20	245.37	0.28810F 03	0.48077F 03
21	270.34	0.28286F 03	0.19791F 03

# FINAL PROFILE

STAGE	TEMP F	VAPOUR RATE MOLES/U.T.	LIQUID RATE MOLES/U.T.
1	215.12	0.	0.26045F 03
2	215.48	0.31254F 03	0.25759F 03
3	216.49	0.30968F 03	0.25411F 03
4	221.42	0.30620F 03	0.24906F 03
5	244.49	0.30115F 03	0.47348F 03
6	244.85	0.32557F 03	0.47111F 03
7	245.22	0.32320F 03	0.46884F 03
8	245.60	0.32093F 03	0.46669F 03
9	245.97	0.31878F 03	0.46466F 03
10	246.33	0.31675F 03	0.46278F 03
11	246.66	0.31487F 03	0.46104F 03
12	246.85	0.31313F 03	0.45956F 03
13	246.30	0.31165F 03	0.45898F 03
14	241.31	0.31107F 03	0.55405F 03
15	241.62	0.30614F 03	0.55203F 03
16	242.06	0.30412F 03	0.54947F 03
17	242.62	0.30156F 03	0.54626F 03
18	243.40	0.29835F 03	0.54231F 03
19	244.77	0.29440F 03	0.53742F 03
20	249.45	0.28951F 03	0.53282F 03
21	275.61	0.28491F 03	0.24791F 03



# PRODUCT STREAM COMPOSITIONS

COMPONENT	CONDENSER STREAM	BOTTOMS STREAM
PHENOL	0.0003	0.7992
CH	0.7852	0.0368
TOLUENE	0.2145	0.1639

RECOVERY OF TOLUENE ACHIEVED = 0.7756





PROBLEM NO. 6  
EXTRACTIVE DISTILLATION  
SYSTEM ACETONE-METHANOL-WATER

A. COLUMN DATA

PRESSURE=ATMOSPHERIC  
NO. OF PLATES=25  
CONDENSER TYPE=TOTAL  
OVERHEAD PRODUCT=23.09  
BOTTOM PRODUCT=575.34  
REFLUX RATIO=4.13  
FEED PLATES= 9,20

B. FEED DATA

TEMPERATURE OF SOLVENT FEED=141.307 F  
RATE OF SOLVENT FEED= 115.56 MOL/U.T.  
TEMPERATURE OF FRESH FEED= 167.71 F  
RATE OF FRESH FEED= 492.87 MOL/U.T.

COMPOSITION IN MOLE FRACTION

COMPONENT	COMPOSITION SOLVENT FEED	COMPOSITION FRESH FEED
ACETONE	0.0000	0.0718
METHANOL	0.0000	0.0972
WATER	1.0000	0.8310

C. EQUILIBRIUM DATA ARE OBTAINED FROM THE SIMPLIFIED  
PRAUSNITZ MODEL USING WILSON'S EQUATION.

THE OPTIMIZED INTERACTION ENERGIES ARE IN CAL/GM. MOLE  
WHERE N=ACETONE M=METHANOL L=WATER

INTERACTION ENERGY(N,L)=-164.879  
INTERACTION ENERGY(L,N)= 1679.652  
INTERACTION ENERGY(N,M)=-315.893  
INTERACTION ENERGY(M,N)= 1719.198  
INTERACTION ENERGY(M,L)= 241.057  
INTERACTION ENERGY(L,M)= 354.830

D. ENTHALPY DATA ARE OBTAINED FROM IDEAL ENTHALPY  
FUNCTIONS WITH HEAT OF SOLUTION CORRECTIONS

THE INFINITE DILUTION HEATS OF SOLUTION ARE IN BTU/LB-MOL  
HEAT OF DIL.(N,M) = HEAT OF DIL.(M,N)= 0.0000  
HEAT OF DIL.(N,L) = HEAT OF DIL.(L,N)= 4520.0  
HEAT OF DIL(M,L) = HEAT OF DIL.(L,M)= 3603.0  
THESE VALUES ARE OBTAINED FROM INTERNATIONAL CRITICAL  
TABLES(32)



## PROBLEM NO. 6

## INITIAL PROFILE

STAGE	TEMP F	VAPOUR RATE MOLES/U.T.	LIQUID RATE MOLES/U.T.
1	122.000	0.	0.1520000E 03
2	122.000	0.1850000E 03	0.1400000E 03
3	122.000	0.1850000E 03	0.1400000E 03
4	122.000	0.1850000E 03	0.1400000E 03
5	122.000	0.1850000E 03	0.1400000E 03
6	122.000	0.1850000E 03	0.1400000E 03
7	140.000	0.1800000E 03	0.1400000E 03
8	140.000	0.1800000E 03	0.2500000E 03
9	140.000	0.1800000E 03	0.2500000E 03
10	140.000	0.1800000E 03	0.2500000E 03
11	140.000	0.1800000E 03	0.2500000E 03
12	140.000	0.1800000E 03	0.2500000E 03
13	140.000	0.1800000E 03	0.2500000E 03
14	140.000	0.1800000E 03	0.2500000E 03
15	158.000	0.1800000E 03	0.2500000E 03
16	158.000	0.1800000E 03	0.2500000E 03
17	158.000	0.1800000E 03	0.2500000E 03
18	158.000	0.1800000E 03	0.2500000E 03
19	158.000	0.1800000E 03	0.2500000E 03
20	176.000	0.1800000E 03	0.7500000E 03
21	176.000	0.1800000E 03	0.7500000E 03
22	176.000	0.1800000E 03	0.7500000E 03
23	176.000	0.1800000E 03	0.7500000E 03
24	176.000	0.1800000E 03	0.7500000E 03
25	176.000	0.1800000E 03	0.7500000E 03



# FINAL PROFILE

STAGE	TEMP F	VAPOUR RATE MOLES/U.T.	LIQUID RATE MOLES/U.T.
1	133.185	C.	0.1366617E 03
2	133.237	0.1697517E 03	0.1364129E 03
3	133.298	0.1695029E 03	0.1361092E 03
4	133.379	0.1691992E 03	0.1357152E 03
5	133.499	0.1688052E 03	0.1351557E 03
6	133.700	0.1682457E 03	0.1342344E 03
7	134.109	0.1673244E 03	0.1321399E 03
8	135.247	0.1652299E 03	0.1192881E 03
9	141.305	0.1523781E 03	0.2484692E 03
10	141.441	0.1659992E 03	0.2481724E 03
11	141.612	0.1657024E 03	0.2478304E 03
12	141.847	0.1653604E 03	0.2473930E 03
13	142.195	0.1649230E 03	0.2467121E 03
14	142.765	0.1642421E 03	0.2454726E 03
15	143.787	0.1630026E 03	0.2432269E 03
16	145.686	0.1607569E 03	0.2397327E 03
17	148.990	0.1572627E 03	0.2353199E 03
18	153.879	0.1528499E 03	0.2304975E 03
19	160.029	0.1480275E 03	0.2253483E 03
20	167.717	0.1428783E 03	0.7354395E 03
21	173.355	0.1600996E 03	0.7353034E 03
22	178.462	0.1599634E 03	0.7355438E 03
23	182.617	0.1602038E 03	0.7350413E 03
24	187.205	0.1597013E 03	0.7330283E 03
25	194.310	0.1576884E 03	0.5753400E 03

SUM (DELTA T\*\*2) AT ITERATION 34 = 0.539





# PRODUCT STREAM COMPOSITIONS

COMPONENT	CONDENSER STREAM	BOTTOM STREAM
ACETONE	0.9637215E 00	0.
METHANOL	0.5497082E-02	0.8346080E-01
WATER	0.3078142E-01	0.9165392E 00

RECOVERY OF METHANOL ACHIEVED = 1.00232



APPENDIX V  
EXAMPLE COMPUTER PROGRAMS

- PROBLEM III
- PROBLEM VI





# \$IBFTC THESIS

```

    DIMENSION T(25),V(25),PROFL(25),G(25),U(25),B(25)
    DIMENSION VK(15,25),E(25),C(25),D(25,15),P(25),Q(25)
    DIMENSION X(15,25),SUMX(25),AT(25),Y(15,25),BBMIX(25)
    DIMENSION ZC(25),AAOB(25),A(17,5),TC(15),PC(15),W(15)
    DIMENSION DELTA(15),V1(15),DDELMX(25),SUMY(25)
98  FORMAT(1H1,44X,13HPROBLEM NO. 3)
99  FORMAT(1X,I2,F5.1,F6.3,F7.3)
100 FORMAT(1HJ,43X,15HINITIAL PROFILE)
101 FORMAT(1HK,20X,5HSTAGE,6X,4HTEMP,10X,11HVAPOUR RATE,8X
    1,11HLIQUID RATE)
102 FORMAT(1X,32X,1HF,12X,10HMOLES/U.T.,10X,10HMOLES/U.T./)
103 FORMAT(1X,20X,I2,6X,F8.3,2(6X,E14.7))
106 FORMAT(1HK,44X,13HFINAL PROFILE)
104 FORMAT(1HK,21X,29HSUM (DELTA T**2) AT ITERATION,1X,I2,
    11X,1H=,F6.3)
105 FORMAT(1X,2F5.1)
110 FORMAT(1X,E14.8)
111 FORMAT(1H1,34X,27HPRODUCT STREAM COMPOSITIONS)
112 FORMAT(1HK,19X,9HCOMPONENT,2X,9HCONDENSER,6X,6HBOTTOM,
    16X,6HVAPOUR,6X,6HLIQUID)
115 FORMAT(1X,32X,7HPRODUCT,6X,7HPRODUCT,4X,10HSIDESTREAM,3X,
    110HSIDESTREAM)
113 FORMAT(1HJ,29X,4(E11.4,2X))
    NP=21
    NCP=11
    NPP=NP-1
    READ(5,99) (J,T(J),V(J),PROFL(J),J=1,NP)
    SW=0.0
    WRITE(6,98)
    WRITE(6,100)
    WRITE(6,101)
    WRITE(6,102)
    DO 901 J=1,NP
901  WRITE(6,103) J,T(J),V(J),PROFL(J)
    DO 13 I=1,NCP
    DO 13 J=1,NP
13  D(J,I)=0.0
C
C  JI IS FEED LOCATION.  D IS FEED COMPOSITION VECTOR IN MOLE
C  PER UNIT TIME
C
    JI=7
    NJ=13
    READ(5,105) ((D(JI,I),D(NJ,I)),I=1,NCP)
    CALL FPTSW
92  IF(SW.EQ.0.0) GO TO 77
    GO TO 123
123 DO 124 J=1,NP
124 CALL CHAOS(T,X,Y,VK,SW,J,BBMIX,ZC,AAOB,A,TC,PC,W,
    1DELTA,V1,DDELMX)
    GO TO 78
77  DO 7 J=1,NP
    DO 7 I=1,NCP
    CALL KVAL(T,VK,I,J,SW)
7  CONTINUE
78  DO 8 J=1,NP
    G(J)=0.0
8  U(J)=0.0
C

```



C U REPRESENTS LIQUID SIDE STREAMS. U(1) IS THE DISTILLATE  
C RATE IN MOLES PER UNIT TIME.

C

```
      C(16)=25.0
      U(4)=15.0
      DO 17 I=1,NCP
      DO 10 J=1,NP
10     R(J)=-((V(J)-S(J))*VK(I,J)+PROFL(J)+U(J))
      E(1)=0.00
      DO 11 J=2,NP
      JJ=J-1
11     E(J)=PROFL(J)
      DO 12 J=1,NPP
12     C(J)=V(J+1)*VK(I,J+1)
      C(NP)=0.00
```

C

C THE ABOVE MATRIX IS SOLVED FOR THE COMPOSITION PROFILE BY  
C A GAUSS ELIMINATION METHOD.

C

```
      P(1)=C(1)/R(1)
      Q(1)=D(1,I)/R(1)
      DO 14 J=2,NPP
14     P(J)=C(J)/(B(J)-(E(J)*P(J-1)))
      P(NP)=0.00
      DO 15 J=2,NP
15     Q(J)=(D(J,I)-(E(J)*Q(J-1)))/(B(J)-(E(J)*P(J-1)))
      X(I,NP)=Q(NP)
      DO 16 J=1,NPP
      L=NP-J
16     X(I,L)=Q(L)-(P(L)*X(I,L+1))
17     CONTINUE
```

C

C COMPOSITION PROFILE IS BEING NORMALIZED

C

```
      DO 19 J=1,NP
      SUMX(J)=0.00
      DO 19 I=1,NCP
      SUMX(J)=SUMX(J)+X(I,J)
19     CONTINUE
      DO 97 J=1,NP
      DO 97 I=1,NCP
      X(I,J)=X(I,J)/SUMX(J)
97     CONTINUE
      DO 75 J=1,NP
      DO 75 I=1,NCP
75     Y(I,J)=VK(I,J)*X(I,J)
      IF(SW.EQ.0.0) GO TO 125
      GO TO 127
125    DO 126 J=1,NP
126    CALL CHAOS(T,X,Y,VK,SW,J,BBMIX,ZC,AAOB,A,TC,PC,W,
1DELTA,V1,DDELMX)
      SW=SW+1.0
      JJJ=SW
      GO TO 78
127    SW=SW+1.0
      JJJ=SW
      CALL TNEW(X,J,AT,SW,Y,T,A,TC,PC,W,DELTA,V1,AAOB,BBMIX,
1ZC,DDELMX)
      DO 131 J=1,NP
      DO 131 I=1,NCP
```





```

131 Y(I,J)=X(I,J)*VK(I,J)
    DO 150 J=1,NP
    SUMY(J)=0.00
    DO 150 I=1,NCP
    SUMY(J)=SUMY(J)+Y(I,J)
150  CONTINUE
    DO 151 J=1,NP
    DO 151 I=1,NCP
    Y(I,J)=Y(I,J)/SUMY(J)
151  CONTINUE
    SUMDT=0.0
    DO 47 J=1,NP
47  SUMDT=SUMDT+(AT(J)-T(J))**2
    IF(SUMDT.LE.1.0) GO TO 37
    GO TO 48
48  DO 49 J=1,NP
    T(J)=AT(J)
49  CALL CHAOS(T,X,Y,VK,SW,J,BBMIX,ZC,AAOB,A,TC,PC,W,
1DELTA,V1,DDELMX)
    CALL PROFYL(V,PROFL,J,X,T,SW,Y,A,TC,PC,W,DELTA,V1,AAOB,
1BBMIX,ZC,DDELMX,NP)
    CALL FPTSW
    GO TO 92
37  WRITE(6,106)
    WRITE(6,101)
    WRITE(6,102)
    DO 904 J=1,NP
904  WRITE(6,103) J,T(J),V(J),PROFL(J)
    WRITE(6,104) JJJ,SUMDT
    WRITE(6,111)
    WRITE(6,112)
    WRITE(6,115)
    DO 903 I=1,11
903  WRITE(6,113) X(I,1),X(I,21),X(I,4),Y(I,16)
    STOP
    END

```





SIBFTC RAY        NODECK,NOLIST

      SUBROUTINE KVAL(T,VK,I,J,SW)

      DIMENSION T(25),VK(15,25),AA(15),AB(15),AC(15)

      DIMENSION ALPHA(15,25)

C

C   THIS SUBROUTINE CALCULATES IDEAL COMPOSITION-INDEPENDENT

C   VAPORIZATION CONSTANTS.

C

101   FORMAT(1X,F8.5,F8.5,F7.5)

      IF(SW.EQ.0.0) GO TO 70

      GO TO 11

70    IF(I.EQ.1.AND.J.EQ.1) GO TO 10

      GO TO 11

10    DO 12 II=1,11

12    READ(5,101) AA(II),AB(II),AC(II)

      AA(9)=-AA(9)

      AA(10)=-AA(10)

      AA(11)=-AA(11)

      AB(1)=-AB(1)

      AB(2)=-AB(2)

      AB(3)=-AB(3)

      AB(4)=-AB(4)

      AB(5)=-AB(5)

      AB(11)=-AB(11)

      AC(7)=-AC(7)

      AC(8)=-AC(8)

11    ALPHA(I,J)=AA(I)+AB(I)\*(T(J)/100.0)+AC(I)\*((T(J)/100.0)\*\*2)

      VK(6,J)=-0.04195+0.34087\*(T(J)/100.0)-0.01815\*((T(J)/100.0)

1\*\*2)+0.02872\*((T(J)/100.0)\*\*3)

      VK(I,J)=VK(6,J)\*ALPHA(I,J)

      RETURN

      END



SIBFTC HELEN NODECK,NOLIST

SUBROUTINE CHAOS(T,X,Y,VK,SW,J,BBMIX,ZC,AAOB,A,TC,PC,  
1W,DELTA,V1,DDELMX)

C

C THIS SUBROUTINE CALCULATES COMPOSITION DEPENDENT K-VALUES  
C BY THE CHAO-SEADER METHOD.

C

DIMENSION T(25),X(15,25),Y(15,25),VK(15,25),A(17,5)  
DIMENSION TC(15),PC(15),W(15),DELTA(15),V1(15),FNU(15,25)  
DIMENSION ARK(15),BRK(15),PHI(15,25),GAM(15,25),VAPL(15,25)  
DIMENSION AAOB(25),BBMIX(25),ZC(25),DDELMX(25),XXF(15,25)  
DIMENSION YYF(15,25),TF(25)

200 FORMAT(1X,40HMORE THAN THIRTY TRIALS ARE REQUIRED FOR,  
114H Z CONVERGENCE)

201 FORMAT(1X,F7.2,F6.1,F6.4,F5.3,F5.1)

199 FORMAT(1X,2E15.8)

NCP=11

IF(SW.EQ.0.0.AND.J.EQ.1) GO TO 299

GO TO 300

299 DO 75 I=1,16

75 READ(5,199) (A(I,IJ),IJ=1,2)

READ(5,201) (TC(I),PC(I),W(I),DELTA(I),V1(I),I=1,NCP)

300 P=250.0

T(J)=T(J)+459.6

DO 101 I=1,NCP

IF(I.EQ.1) GO TO 11

IF(I.GT.1) GO TO 12

11 IJ=1

GO TO 14

12 IJ=2

GO TO 14

14 TR=T(J)/TC(I)

PR=P/PC(I)

FPO=A(1,IJ)+A(2,IJ)/TR+A(3,IJ)\*TR+A(4,IJ)\*TR\*\*2+A(5,IJ)\*TR\*\*3  
1+(A(6,IJ)+A(7,IJ)\*TR+A(8,IJ)\*TR\*\*2)\*PR+(A(9,IJ)+A(10,IJ)\*TR)  
1\*PR\*\*2-ALOG(PR)/2.30258

FPI=(A(11,IJ)+A(12,IJ)\*TR+A(13,IJ)/TR+A(14,IJ)\*TR\*\*3+A(15,IJ)  
1\*(PR-0.6))

101 FNU(I,J)=(FPO+W(I)\*FPI)\*2.30258

AMIX=0.0

BMIX=0.0

DO 102 I=1,NCP

TR=T(J)/TC(I)

ARK(I)=(0.4278/(PC(I)\*TR\*\*2.5))\*\*0.5

BRK(I)=0.0867/(PC(I)\*TR)

BMIX=BMIX+BRK(I)\*Y(I,J)

102 AMIX=AMIX+ARK(I)\*Y(I,J)

AOR=AMIX\*AMIX/BMIX

CON1=2.0

CON2=BMIX\*P+0.001

DO 106 KK=1,30

ZAS=(CON1+CON2)/2.0

H=BMIX\*P/ZAS

Z=1.0/(1.0-H)-AOB\*(H/(1.0+H))

DEL=Z-ZAS

IF(ABS(DEL).LE.1.0E-04) GO TO 107

IF(DEL.LT.0.0) GO TO 104

IF(DEL.GT.0.0) GO TO 105

104 CON1=ZAS

GO TO 106





```

105 CON2=ZAS
106 CONTINUE
107 AAOB(J)=AOB
    BRMIX(J)=BMIX
    ZC(J)=Z
    DO 108 I=1,NCP
108  PHI(I,J)=(Z-1.0)*(BRK(I)/BMIX)-ALOG(Z-BMIX*P)-AOB*((2.0*
    1ARK(I))/AMIX-(BRK(I)/BMIX))*ALOG(1.0+H)
    C1=0.0
    C2=0.0
    DO 109 I=1,NCP
    DELMX=X(I,J)*V1(I)
    C1=C1+DELMX
109  C2=C2+DELMX*DELTA(I)
    DELMX=C2/C1
    DDELMX(J)=DELMX
    C1=1.987*T(J)/1.8
    DO 110 I=1,NCP
    GAM(I,J)=V1(I)*(DELTA(I)-DELMX)**2/C1
    VAPL(I,J)=(FNU(I,J)+GAM(I,J)-PHI(I,J))
110  VK(I,J)=EXP(VAPL(I,J))
    T(J)=T(J)-459.6
    RETURN
    END

```



\$IBFTC EDWARD NODECK,NOLIST

```
SUBROUTINE TNEW(X,J,AT,SW,Y,T,A,TC,PC,W,DELTA,V1,AAOB,  
1BRMIX,ZC,DDELMX)  
  DIMENSION TT(25),T(25),AT(25),X(15,25),VK(15,25),D(25)  
  DIMENSION S(20,20),SUMY(25),Y(15,25),XY(25),A(17,5)  
  DIMENSION TC(15),PC(15),W(15),DELTA(15),V1(15),AAOB(25)  
  DIMENSION BRMIX(25),ZC(25),DDELMX(25)
```

C  
C THIS SUBROUTINE USES MULLER,S QUADRATIC ROOTS METHOD TO  
C CALCULATE THE NEW TEMPERATURE PROFILE.  
C

```
  NCP=11  
  J=1  
57  JJ=1  
  YXX=T(J)  
  YX=YXX  
14  FJJ=JJ-1  
  TT(JJ)=(T(J)-10.0)+FJJ*10.0  
  XY(J)=TT(JJ)  
  CALL CHAOS(XY,X,Y,VK,SW,J,BBMIX,ZC,AAOB,A,TC,PC,W,  
1DELTA,V1,DDELMX)  
  SUMY(J)=0.00  
  DO 12 I=1,NCP  
12  SUMY(J)=SUMY(J)+VK(I,J)*X(I,J)  
  S(J,JJ)=SUMY(J)-1.00  
  JJ=JJ+1  
  IF(JJ.EQ.4) GO TO 19  
  GO TO 14  
19  K=4  
  KIK=1  
99  D(K-1)=(TT(K-1)-TT(K-2))/(TT(K-2)-TT(K-3))  
  B=S(J,K-3)*(D(K-1)**2)-S(J,K-2)*(1.0+D(K-1))**2+S(J,  
1K-1)*(1.0+(2.*D(K-1)))  
  C=S(J,K-3)*D(K-1)-S(J,K-2)*(1.0+D(K-1))+S(J,K-1)  
  E=-2.0*S(J,K-1)*(1.0+D(K-1))  
  AA=B**2-4.0*S(J,K-1)*D(K-1)*(1.0+D(K-1))*C  
  ABP=B+(ABS(AA)**0.5)  
  ABM=B-(ABS(AA)**0.5)  
  BC1=E/ABP  
  BC2=E/ABM  
  TA=TT(K-1)+(TT(K-1)-TT(K-2))*BC1  
  TB=TT(K-1)+(TT(K-1)-TT(K-2))*BC2  
  IF(TA.GT.1000.0.AND.TB.GT.1000.0) GO TO 120  
  IF(TA.LT.0.00.AND.TB.GT.1000.0) GO TO 120  
  IF(TA.GT.1000.0.AND.TB.LT.0.00) GO TO 120  
  IF(TA.LT.0.00.AND.TB.LT.0.00) GO TO 120  
  IF(TA.LT.0.0.OR.TA.GT.1000.0) GO TO 70  
  GO TO 87  
120 TA=YX  
  GO TO 98  
87  T(J)=TA  
  CALL CHAOS(T,X,Y,VK,SW,J,BBMIX,ZC,AAOB,A,TC,PC,W,  
1DELTA,V1,DDELMX)  
  SUMY(J)=0.00  
  DO 81 I=1,NCP  
81  SUMY(J)=SUMY(J)+VK(I,J)*X(I,J)  
  SA=SUMY(J)-1.00  
  IF(TB.LT.0.0.OR.TB.GT.1000.0) GO TO 92  
  GO TO 70  
70  T(J)=TB
```



CALL CHAOS(T,X,Y,VK,SW,J,BRMIX,ZC,AAOB,A,TC,PC,W,  
1DELTA,V1,DDELMX)

SUMY(J)=0.0

DO 83 I=1,NCP

83 SUMY(J)=SUMY(J)+VK(I,J)\*X(I,J)

SB=SUMY(J)-1.00

IF(ABS(SB).LT.ABS(SA)) GO TO 91

GO TO 92

91 IF(ABS(SB).LE.0.001) GO TO 97

K=K+1

TT(K-1)=TB

S(J,K-1)=SB

KIK=KIK+1

IF(KIK.EQ.20) GO TO 120

GO TO 99

92 IF(ABS(SA).LE.0.001) GO TO 98

K=K+1

TT(K-1)=TA

S(J,K-1)=SA

KIK=KIK+1

IF(KIK.EQ.20) GO TO 120

GO TO 99

97 AT(J)=TB

T(J)=YXX

GO TO 15

98 AT(J)=TA

T(J)=YXX

GO TO 15

15 IF(J.EQ.21) GO TO 56

GO TO 58

58 J=J+1

GO TO 57

56 RETURN

END





SIBFTC COUTU NODECK,NOLIST

SUBROUTINE ENTHAL(Y,X,T,BBMIX,ZC,AAOB,A,TC,PC,EV,EL,SW,  
1V1,DDELMX,DELTA,J,W)

C  
C THIS SUBROUTINE CALCULATES THE LIQUID AND VAPOR STREAM  
C ENTHALPIES BY THE CHAO-SEADER METHOD.  
C

```

      DIMENSION TC(15),PC(15),A(17,5),HFC(15),HAC(15),V1(15)
      DIMENSION DELTA(15),DDELMX(25),HL(15),T(25),W(15),EV(25)
      DIMENSION EL(25),CH(15),XXF(15,25),YYF(15,25),TF(25),TT(25)
      DIMENSION HIDL(15),AH(15),BH(15),DH(15),Y(15,25)
      DIMENSION B(15,25),BBMIX(25),ZC(25),AAOB(25),X(15,25)
      TT(J)=T(J)+459.6
101  FORMAT(1X,4E14.7)
105  FORMAT(1X,I2,2(2X,F10.3))
      P=250.0
      NCP=11
      IF(SW.EQ.2.0.AND.J.EQ.1) GO TO 99
      GO TO 100
99  READ(5,101) (AH(I),BH(I),CH(I),DH(I),I=1,NCP)
100  DO 1 I=1,NCP
1   HIDL(I)=AH(I)+BH(I)*T(J)+CH(I)*T(J)**2+DH(I)*T(J)**3
      SUMHV=0.0
      DO 3 I=1,NCP
3   SUMHV=SUMHV+Y(I,J)*HIDL(I)
      H=BBMIX(J)*P/ZC(J)
      HVC=(1.5*AAOB(J)*ALOG(1.0+H)+1.0-ZC(J))*1.987*TT(J)
      EV(J)=SUMHV-HVC
      SUMHL=0.0
      DO 4 I=1,NCP
      IF(I.EQ.1) GO TO 11
      IF(I.GT.1) GO TO 12
11  IJ=1
      GO TO 16
12  IJ=2
      GO TO 16
16  TR=TT(J)/TC(I)
      PR=P/PC(I)
      CON1=-A(2,IJ)/TR**2+A(3,IJ)+2.0*A(4,IJ)*TR+3.0*A(5,IJ)
1*TR**2+(A(7,IJ)+2.0*A(8,IJ)*TR)*PR+A(10,IJ)*PR**2+(A(12
2,IJ)-A(13,IJ)/TR**2+3.0*A(14,IJ)*TR**2)*W(I)
      CON1=CON1*2.30258/TC(I)
      HFC(I)=CON1
      HAC(I)=-((V1(I)*(DELTA(I)-DDELMX(J))**2)/(1.987*(TT(J)
1**2)))*1.8
      HL(I)=-(HFC(I)+HAC(I))*1.987*TT(J)**2+HIDL(I)
4   SUMHL=SUMHL+X(I,J)*HL(I)
      EL(J)=SUMHL
      T(J)=TT(J)-459.6
      RETURN
      END
```



```
$IBFTC KATHY    NODECK,NOLIST
      SUBROUTINE PROFYL(V,PROFL,J,X,T,SW,Y,A,TC,PC,W,DELTA,V1,
      1AAOB,BBMIX,ZC,DDELMX,NP)
```

```
C
C THIS SUBROUTINE CALCULATES NEW VAPOR AND LIQUID PROFILES
C BY MAKING CONVENTIONAL ENTHALPY BALANCES.
```

```
C
      DIMENSION FEV(25),FEL(25),Y(15,25),SUMY(25),T(25)
      DIMENSION SH(15,25),CH(15,25),EV(25),EL(25),X(15,25)
      DIMENSION V(25),PROFL(25),F(25),Q(25),P(25),U(25),HF(25)
      DIMENSION EF1(15),EF2(15),VK(15,25),A(17,5),TC(15),PC(15)
      DIMENSION W(15),DELTA(15),V1(15),AAOB(25),BBMIX(25)
      DIMENSION ZC(25),DDELMX(25),TF(25),XXF(15,25),YYF(15,25)
105  FORMAT(1X,I2,2(2X,F10.3))
106  FORMAT(1X,F7.5)
108  FORMAT(1X,1HJ,5X,1HT,7X,1HV,7X,1HL)
109  FORMAT(1X,I2,1X,F7.2,1X,F7.2,1X,F7.2)
      NP=21
      NCP=11
      NPP=NP-1
      IF(SW.EQ.2.0) GO TO 71
      GO TO 70
71  DO 85 I=1,NCP
      DO 85 J=1,NP
      XXF(I,J)=0.0
85  YYF(I,J)=0.0
      DO 69 I=1,NCP
      J=13
69  READ(5,106) XXF(I,J)
75  DO 76 I=1,NCP
      J=7
76  READ(5,106) YYF(I,J)
70  DO 19 J=1,NP
      SUMY(J)=0.00
      DO 19 I=1,NCP
19  SUMY(J)=SUMY(J)+Y(I,J)
      DO 67 J=1,NP
      DO 67 I=1,NCP
67  Y(I,J)=Y(I,J)/SUMY(J)
      DO 74 J=1,NP
74  CALL ENTHAL(Y,X,T,BBMIX,ZC,AAOB,A,TC,PC,EV,EL,SW,V1,
      1DDELMX,DELTA,J,W)
      V(1)=23.0
      V(2)=94.806
      PROFL(1)=71.806
      PROFL(21)=37.0
      DO 51 J=1,NP
      F(J)=0.00
      TF(J)=0.0
      Q(J)=0.00
      P(J)=0.0
      U(J)=0.00
51  HF(J)=0.0
      F(7)=34.50
      F(13)=65.50
      U(4)=15.0
      P(16)=25.0
      J=7
      TF(7)=117.7
      CALL CHAOS(TF,XXF,YYF,VK,SW,J,BBMIX,ZC,AAOB,A,TC,PC,W,
```







```

1 DELTA,V1,DDFLMX)
  CALL ENTHAL(YYF,XXF,TF,BBMIX,ZC,AAOB,A,TC,PC,FEV,FEL,
1 SW,V1,DDELMX,DELTA,J,W)
  J=13
  TF(13)=268.5
  CALL CHAOS(TF,XXF,YYF,VK,SW,J,BBMIX,ZC,AAOB,A,TC,PC,W,
1 DELTA,V1,DDELMX)
  CALL ENTHAL(YYF,XXF,TF,BBMIX,ZC,AAOB,A,TC,PC,FEV,FEL,
1 SW,V1,DDFLMX,DELTA,J,W)
  HF(7)=FFV(7)
  HF(13)=FEL(13)
  DO 115 J=2,NPP
  XBX=(EL(J-1)-EL(J))*PROFL(J-1)
  BXX=(EL(J)-EV(J))*(V(J)+P(J))
  BBX=(HF(J)-EL(J))*F(J)
  BBB=(FL(J)-EV(J+1))
  BBV=(XBX+BXX+BBX-Q(J))/BBB
  BAB=ABS((BBV-V(J+1))/V(J+1))
  IF(BBV.LE.0.0.OR.BAB.GE.0.40) GO TO 110
  GO TO 111
110 V(J+1)=V(J+1)
  GO TO 112
111 V(J+1)=BBV
  GO TO 112
112 BBL=F(J)+PROFL(J-1)+V(J+1)-V(J)-P(J)-U(J)
  ABA=ABS((BBL-PROFL(J))/PROFL(J))
  IF(BBL.LE.0.0.OR.ABA.GE.0.40) GO TO 113
  GO TO 114
113 PROFL(J)=PROFL(J)
  GO TO 115
114 PROFL(J)=BBL
  GO TO 115
115 CONTINUE
  RETURN
  END

```



Cards to be changed when problem III is used with a different system:

Mainline Program (Thesis)

1. The number of plates  $NP = 21$
2. The number of components  $NCP = 11$
3. The locations of the feeds  $J1 = 7$   
 $NJ = 13$
4. The locations and flow rates of the vapor and liquid side-streams respectively  $6(16) = 25.0$   
 $U(4) = 15.0$

\$ IBFTC Helen

Chao-Seader Subroutine

1. The number of components  $NCP = 11$
2. The column pressure, atm.  $P = 250.0$

Temperatures coming into this subroutine have to be in  $^{\circ}\text{F}$ .

\$ IBFTC Edward

Subroutine for new temperatures

1. Number of plates  $\text{IF}(J.EQ. 21) \text{ GO to } 56.$

\$ IBFTC Coutu

Subroutine for enthalpy calculations

1. Column pressure, atms.  $P = 250.0$
2. Number of components  $NCP = 11$



\$ IBFTC Kathy

Subroutine for new rates

1. Number of plates	NP	=	21
2. Number of components	NCP	=	11
3. Liquid feed introduction, moles/U.T.	J	=	13
4. Vapor feed introduction, moles/U.T.	J	=	7
5. Top vapor product, moles/U.T.	V(1)	=	23.0
6. Condenser input, moles/U.T.	V(2)	=	94.806
7. Condenser recycle stream, L <sub>1</sub>	PROFL(1)	=	71.806
8. Bottom product	PROFL(21)	=	37.0
9. Feed locations and rates	F(7)	=	34.50
10. Sidestream locations and rates	U(4)	=	15.0
	P(16)	=	25.0
11. Feed temperatures and locations	J	=	7
	TF(7)	=	117.7
	J	=	13
	TF(13)	=	268.5
12. Setting of feed enthalpies to the calculated ones			
	HF(7)	=	FEV(7)
	HF(13)	=	FEL(13)

Data Cards to be Changed

1. Initial Profile

X01080.023.000071.806

Format (IX, I2, F5.1, F6.3, F7.3)

Stage number = I2 = 01

Temperature = F5.1 = 080.0°F





Vapor rate = F6.3 = 23.000 moles/U.T.

Liquid rate = F7.3 = 071.806 moles/U.T.

2. Distribution of components in the two feeds

X-02.0-00.0

Format (IX, 2F 5.1)

The rate of introduction of first component is:

2.0 moles/U.T. in first feed

0.0 moles/U.T. in second feed

The next card represents the rate of introduction of second component.

Negative signs arise from the setting of the matrix solutions  $(-F_j Z_{ij})$

3. Equilibrium data for first iteration

In this case, relative volalities are calculated and component six is the reference component.

4. Chao-Seader data for the components in the system

X0343.900673.10.00005.680052.0

Format (IX, F7.2, F6.1, F6.4, F5.3, F5.1)

Critical temperature  $^{\circ}\text{R}$  = F7.2 = 0343.90

Critical pressure, psi = F6.1 = 0673.1

Acentric factor = F6.4 = 0.0000



$\delta_i$  = F5.3 = 5.680

volume parameter  $V_i$  = F5.1 = 052.0

This information is for component 1 only.

5. Composition of the feeds

X0.00000

Format (IX, F7.5)

This means that in the first feed, there is none of component 1.

The composition of the first feed is read in for every component then that of the second.

6. The parameters for the Chao-Seader component enthalpies

Format (IX, 4E 14.7)

AH, BH, CH, DH are listed by component





91 RETC THESIS NODECK

COMMON J,IW,NP,NCP,KK,IK,FLOD,I

COMMON V(25),PROFL(25),VK(15,25),Y(15,25)

COMMON SUMX(25),Y(15,25),PRMIX(25),ZC(25),ΔAOR(25)

COMMON A(17,5),DELTA(15),V1(15),DDELHX(25),F(25),U(25)

DIMENSION G(25),P(25),F(25),C(25),P(25),Q(25),AT(25),  
ID(25),T(25)

98 FORMAT(1H1,44X,13HPROBLEM NO. 6)

99 FORMAT(1X,12,F5.1,F5.1,F5.1)

100 FORMAT(1HJ,42X,15HINITIAL PROFILE)

101 FORMAT(1HK,20X,5HSTAGE,6X,4HTEMP,10X,11HVAPOUR RATE,8X  
1,11HLIQUID RATE)

102 FORMAT(1X,32X,1HF,12X,10HMOLES/U.T.,10X,10HMOLES/U.T./)

103 FORMAT(1X,20X,12,6X,F8.3,2(6X,F14.7))

104 FORMAT(1HK,21X,20HSUM (DELTA T\*\*2) AT ITERATION,1X,12,  
11X,1H=,F6.3)

106 FORMAT(1HK,44X,13HFINAL PROFILE)

111 FORMAT(1H1,31X,27HPRODUCT STREAM COMPOSITIONS)

112 FORMAT(1HK,22X,9HCOMPONENT,3X,16HCONDENSER STREAM,6X,1  
13HBOTTOM STREAM)

113 FORMAT(1HJ,34X,F14.7,7X,E14.7)

114 FORMAT(1HK,30X,31HRECOVERY OF METHANOL ACHIEVED =,F8.5)

116 FORMAT(1H1)

NCP=3

NP=25

NPP=NP-1

DO 8 J=1,NP

G(J)=0.0

F(J)=0.0

8 U(J)=0.0

C

C INITIAL PROFILE IS READ IN

C

READ(5,99) (J,T(J),PROFL(J),V(J),J=1,NP)

DO 200 J=1,NP

200 T(J)=(T(J)\*1.8)+32.0

C

C KK IS SOLVENT FEED LOCATION. IK IS FRESH FEED LOCATION.

C F IS FEED RATE IN MOLES/U.T.. FLOD IS L/D RATIO. U(1) IS

C DISTILLATE RATE.

C

WRITE(6,98)

WRITE(6,100)

WRITE(6,101)

WRITE(6,102)

DO 901 J=1,NP

901 WRITE(6,103) J,T(J),V(J),PROFL(J)

KK=9

IK=20

F(KK)=115.56

F(IK)=492.87

U(1)=33.09

FLOD=4.13

IW=0

92 IF(IW.EQ.0) GO TO 77

GO TO 65

65 DO 66 J=1,NP

66 CALL WILSON(T)

GO TO 78



```

77 DO 7 J=1,NP
   DO 7 I=1,NCP
   CALL KVAL(T)
7   CONTINUE
78 DO 17 I=1,NCP
   DO 10 J=1,NP
10  R(J)=-((V(J)+G(J))*VK(I,J)+(PROFL(J)+U(J)))
   F(1)=0.00
   DO 11 J=2,NP
   JJ=J-1
11  F(J)=PROFL(JJ)
   DO 12 J=1,NPP
12  C(J)=V(J+1)*VK(I,J+1)
   C(NP)=0.00
   DO 13 J=1,NP
13  D(J)=0.00

```

C  
C I REPRESENTS THE COMPONENT. D IS THE COMPOSITION OF THE  
C PARTICULAR FEED IN MOLES OF COMPONENT I PER UNIT TIME.  
C FOR EXAMPLE, THE SOLVENT FEED HAS NONE OF COMPONENT 1  
C (ACETONE) AND THE FRESH FEED HAS 0.0718 MOLES OF ACETONE  
C PER MOLE OF FEED  
C

```

   IF(I.EQ.1) GO TO 61
   IF(I.EQ.2) GO TO 62
   IF(I.EQ.3) GO TO 63
   GO TO 91
61  D(KK)=-F(KK)*0.0
   D(IK)=-F(IK)*0.0718
   GO TO 91
62  D(KK)=-0.0
   D(IK)=-F(IK)*0.0972
   GO TO 91
63  D(KK)=-F(KK)*1.00
   D(IK)=-F(IK)*0.8310
   GO TO 91
91  POT=F(KK)+F(IK)-U(1)
   P(1)=C(1)/R(1)
   Q(1)=D(1)/R(1)
   DO 14 J=2,NPP
14  P(J)=C(J)/(R(J)-(F(J)*P(J-1)))
   P(NP)=0.00
   DO 15 J=2,NP
15  Q(J)=(D(J)-(F(J)*Q(J-1)))/(R(J)-(F(J)*P(J-1)))
   X(I,NP)=Q(NP)
   DO 16 J=1,NPP
   L=NP-J
16  X(I,L)=Q(L)-(P(L)*X(I,L+1))
17  CONTINUE
   IF(IW.GE.4) GO TO 303
   GO TO 302

```

C  
C THE ACETONE CONTENT IN THE TWO BOTTOM-MOST STREAM IS SET  
C TO ZERO TO INDUCE CONVERGENCE.

```

302 X(1,NPP)=0.0000
   X(1,NP)=0.0000

```

C  
C THE COMPOSITION PROFILE IS BEING NORMALIZED.  
C





```

302 DO 19 J=1,NP
    SUMX(J)=0.00
    DO 19 I=1,NCP
        SUMX(J)=SUMX(J)+X(I,J)
19 CONTINUE
    DO 97 J=1,NP
        DO 97 I=1,NCP
            X(I,J)=X(I,J)/SUMX(J)
97 CONTINUE
    IF(IW.EQ.0) GO TO 69
    GO TO 71
69 DO 70 J=1,NP
70 CALL WILSON(T)
    IW=IW+1
    JJJ=IW
    GO TO 78
71 IW=IW+1
    JJJ=IW
    IF(JJJ.EQ.70) GO TO 59
    GO TO 211
211 CALL TNEW(AT)
    SUMDT=0.0
    DO 47 J=1,NP
47 SUMDT=SUMDT+(AT(J)-T(J))*2
    IF(SUMDT.LE.1.0) GO TO 38
    GO TO 48
48 DO 49 J=1,NP
49 T(J)=AT(J)
    CALL PROFYL(T)
    GO TO 65
38 RECT=X(2,NP)*ROT/47.907
    WRITE(6,116)
    WRITE(6,106)
    WRITE(6,101)
    WRITE(6,102)
    DO 902 J=1,NP
902 WRITE(6,103) J,T(J),V(J),PROFL(J)
    WRITE(6,104) IW,SUMDT
    WRITE(6,111)
    WRITE(6,112)
    DO 903 I=1,NCP
903 WRITE(6,113) X(I,1),X(I,NP)
    WRITE(6,114) RECT
59 STOP
END

```





51 RETC RAY

```
SUBROUTINE KVAL(T)
COMMON J, IW, NP, MCP, KV, TK, FLOD, I
COMMON V(25), PROFL(25), VK(15,25), X(15,25)
COMMON SUMX(25), Y(15,25), RBMIX(25), ZC(25), AAOR(25)
COMMON A(17,5), DELTA(15), V1(15), DDFLMX(25), F(25), II(25)
DIMENSION FN1(10,25), T(25)
```

C  
C THIS SUBROUTINE CALCULATES COMPOSITION-INDEPENDENT VAPO-  
C RIZATION CONSTANTS FROM THE CHAO-SEADER MODEL BY ASSUMING  
C  $K(I,J)=F/P$  RATIO FOR THE LIQUID PHASE.

C

```
P=14.7
A0=5.75748
A1=-3.01761
A2=-4.98500
A3=2.02299
A4=0.00
A5=0.08427
A6=0.26667
A7=-0.31138
A8=-0.02655
A9=0.02883
A10=-4.23893
A11=8.65808
A12=-1.22060
A13=-3.15224
A14=-0.025
IF(I.EQ.1) GO TO 11
IF(I.EQ.2) GO TO 12
IF(I.EQ.3) GO TO 13
```

11 TC=914.0

```
W=0.5169
PC=690.0
GO TO 16
```

12 TC=923.0

```
W=0.599
PC=1156.4
GO TO 16
```

13 TC=1164.2

```
W=0.6576
PC=3200.2
GO TO 16
```

16 TR=(T(J)+459.0)/TC

```
PR=P/PC
```

```
FP1=A0+A1/TR+A2*TR+A3*(TR**2)+A4*(TR**3)+(A5+A6*TR+A7*(TR**2))*PR-  
1 (A8+A9*TR)*(PR**2)-ALOG(PR)/2.30258
```

```
FP2=A10+(A11*TR)+(A12/TR)+(A13*(TR**3))+(A14*(PR-0.6))
```

```
FN1(I,J)=(FP1+W*FP2)*2.30258
```

```
VK(I,J)=EXP(FN1(I,J))
```

```
RETURN
```

```
END
```



SUBROUTINE WILSON(T)

COMMON J,IW,NP,NCP,KK,JK,FLOD,I

COMMON V(25),PROFL(25),VK(15,25),X(15,25)

COMMON SUMX(25),Y(15,25),R3MX(25),ZC(25),AAOR(25)

COMMON A(17,5),DELTA(15),V1(15),DDFLMX(25),F(25),U(25)

DIMENSION ALAMDA(3,3),Z(25),C(25),RHO(15),B(15),WILSPR

1(15,15),G(15,25),GAMMA(15,25),VP(15,25),SUMY(25),CDELY

2(15),SUM1(15),SUM2(15),SUM3(15),T(25)

C

C THIS SUBROUTINE CALCULATES COMPOSITION-DEPENDENT VAPORI-  
C ZATION CONSTANTS USING THE SIMPLIFIED PRAUSNITZ EQUILI-  
C BRIUM MODEL WITH LIQUID ACTIVITY COEFFICIENTS CALCULATED  
C BY THE WILSON MODEL

C

C

C COMPONENT 1 IS ACETONE, 2 IS METHANOL, 3 IS WATER.

C

DO 7 JI=1,NCP

DO 7 IJ=1,NCP

7 ALAMDA(JI,IJ)=0.0

N=1

M=2

L=3

C

C ALAMDA IS THE BINARY INTERACTION ENERGIES IN CAL/GM-MOLE  
C OBTAINED FROM ONE OF THE OPTIMIZATION TECHNIQUES

C

ALAMDA(N,L)=-164.879

ALAMDA(L,N)=1679.652

ALAMDA(N,M)=-315.893

ALAMDA(M,N)=719.198

ALAMDA(M,L)=241.057

ALAMDA(L,M)=354.830

C(J)=(T(J)-32.0)/1.8

Z(J)=C(J)+272.16

C

C RHO IS THE DENSITY CALCULATED BY EQUATIONS OFTEN REPORTED  
C IN THE CRITICAL TABLES. B IS THE MOLAR VOLUME OF THE  
C COMPONENTS (MOLE WT/DENSITY)

C

RHO(N)=0.81248-1.100\*C(J)\*(10.\*\*(-2))-0.859\*(C(J)\*\*2)\*  
1(10.\*\*(-6))

RHO(M)=0.792

RHO(L)=1.000

P(N)=58.046/RHO(N)

P(M)=32.031/RHO(M)

P(L)=18./RHO(L)

C

C WILSPR IS THE BINARY WILSON CONSTANTS.

C

DO 12 II=1,NCP

DO 12 JI=1,NCP

WILSPR(II,JI)=B(JI)/(B(II)\*EXP(ALAMDA(II,JI)/(1.9870\*Z  
1(J))))

12 CONTINUE

C

C TP IS TOTAL PRESSURE IN MM-HG.

C







TP=767.0

C

C THE FOLLOWING IS THE CALCULATION OF THE LIQUID PHASE  
C ACTIVITY COEFFICIENTS ACCORDING TO THE WILSON EQUATION.  
C

II=1

```
21 SUM1(II)=0.0
   DO 17 JI=1,NCP
17 SUM1(II)=SUM1(II)+X(JI,J)*WILSPR(II,JI)
   DO 19 III=1,NCP
   SUM2(III)=0.0
   DO 18 JI=1,NCP
18 SUM2(III)=SUM2(III)+X(JI,J)*WILSPR(III,JI)
19 SUM3(III)=(X(III,J)*WILSPR(III,II))/SUM2(III)
   SUM=0.0
   DO 20 JJJ=1,NCP
20 SUM=SUM+SUM3(JJJ)
   G(II,J)=-ALOG(SUM1(II))+1.0-SUM
   IF(II.EQ.NCP) GO TO 22
   II=II+1
   GO TO 21
22 DO 23 II=1,NCP
   GAMMA(II,J)=EXP(G(II,J))
23 CONTINUE
```

C

C VP IS THE VAPOR PRESSURE CALCULATED BY THE ANTOINE EQUA-  
C TION AND REPORTED IN STANDARD HANDBOOKS.  
C

```
VP(N,J)=EXP(2.30258*(7.02447-(1161.0/(224.0+C(J))))))
VP(M,J)=EXP(2.30258*(7.87862-(1472.11/(230.0+C(J))))))
VP(L,J)=EXP(2.30258*(7.96681-(1668.21/(228.0+C(J))))))
DO 26 I=1,NCP
26 Y(I,J)=X(I,J)*GAMMA(I,J)*VP(I,J)/TP
DO 25 I=1,NCP
25 VK(I,J)=Y(I,J)/X(I,J)
RETURN
END
```



SIRFEC FORWARD

```

SUBROUTINE TNEW(AT)
COMMON J,IW,NP,NCP,KK,IK,ELOD,I
COMMON V(25),PROFL(25),VK(15,25),Y(15,25)
COMMON SUMX(25),Y(15,25),PRMIX(25),ZC(25),AAOR(25)
COMMON A(17,5),DELTA(15),V1(15),DDFLMX(25),F(25),U(25)
DIMENSION TT(25),AT(25),D(25),S(20,20),SUMY(25),GAMMA(
115,25),T(25)
J=1
57 JJ=1
14 N=JJ
TT(JJ)=(0.5*0+0.5)*100.0
T(J)=TT(JJ)
CALL WILSON(T)
SUMY(J)=0.00
DO 12 I=1,NCP
12 SUMY(J)=SUMY(J)+VK(I,J)*X(I,J)
S(J,JJ)=SUMY(J)-1.00
JJ=JJ+1
IF(JJ.EQ.4) GO TO 19
GO TO 14
19 K=4
99 D(K-1)=(TT(K-1)-TT(K-2))/(TT(K-2)-TT(K-3))
R=S(J,K-2)*(D(K-1)**2)-S(J,K-2)*(1.0+D(K-1))**2+S(J,K-1)*(1.0+(2.
1D(K-1)))
C=S(J,K-2)*D(K-1)-S(J,K-2)*(1.0+D(K-1))+S(J,K-1)
OO=-2.0*S(J,K-1)*(1.0+D(K-1))
AA=(ABS(R)**2)-4.0*S(J,K-1)*D(K-1)*(1.0+D(K-1))*C
ARP=R+(ABS(AA)**0.5)
ABM=B-(ABS(AA)**0.5)
RC1=OO/ARP
RC2=OO/ABM
TA=TT(K-1)+(TT(K-1)-TT(K-2))*RC1
TB=TT(K-1)+(TT(K-1)-TT(K-2))*RC2
IF(TA.GT.0.0) GO TO 69
GO TO 70
69 T(J)=TA
CALL WILSON(T)
SUMY(J)=0.00
DO 81 I=1,NCP
81 SUMY(J)=SUMY(J)+Y(I,J)
SA=SUMY(J)-1.00
IF(TB.LT.0.0) GO TO 92
GO TO 70
70 T(J)=TB
CALL WILSON(T)
SUMY(J)=0.0
DO 83 I=1,NCP
83 SUMY(J)=SUMY(J)+Y(I,J)
SB=SUMY(J)-1.00
IF(ABS(SB).LT.ABS(SA)) GO TO 91
GO TO 92
91 IF(ABS(SB).LE.0.0001) GO TO 97
TT(K-1)=TB
S(J,K-1)=SB
GO TO 99
92 IF(ABS(SA).LE.0.0001) GO TO 98
TT(K-1)=TA
S(J,K-1)=SA

```





```
GO TO 99
97 AT(J)=TR
GO TO 15
98 AT(J)=TA
GO TO 15
15 IF(J.EQ.NP) GO TO 56
GO TO 58
58 J=J+1
GO TO 57
56 RETURN
END
```





51PFTC KATHY

SUBROUTINE PROFYL(T)

COMMON J,IW,NP,NCP,KK,IF,FLDD,I

COMMON V(25),PROFL(25),VK(15,25),X(15,25)

COMMON SUMX(25),Y(15,25),PRMIX(25),ZC(25),AAOR(25)

COMMON A(17,5),DELTA(15),V1(15),DDFLMX(25),F(25),II(25)

DIMENSION SUMY(25),SH(15,25),CH(15,25),EV(25),FL(25),Q  
1(25),HEATDL(15,15),FXL1(15,25),FXL2(15,25),FXCSHT(15,2  
25),XF(15,25),HF(25),G(25),T(25)

C

C W,S ARE MOLECULAR WEIGHTS

C

W1=58.046

W2=32.031

W3=18.0

DO 73 I=1,NCP

DO 73 II=1,NCP

73 HEATDL(I,II)=0.00

C

C HEATDL ARE HEATS OF SOLUTION AT INFINITE DILUTION IN

C BTU/LB-MOLF OBTAINED FROM THE CRITICAL TABLES.

C

HEATDL(1,3)=4520.0

HEATDL(3,1)=4520.0

HEATDL(2,3)=3603.0

HEATDL(3,2)=3603.0

C

C THE FOLLOWING IS THE CALCULATION OF PARTIAL MOLAR HEATS

C OF SOLUTION AT THE PLATE COMPOSITIONS USING EQUATION

C 11-22 IN B.D.SMITH.

C

DO 98 J=1,NP

DO 98 I=1,NCP

FXL1(I,J)=0.0

DO 98 IJ=1,3

FXL1(I,J)=X(IJ,J)\*(HEATDL(IJ,I)+HEATDL(I,IJ))+FXL1(I,J  
1)

98 CONTINUE

DO 99 J=1,NP

DO 99 I=1,NCP

FXL2(I,J)=0.0

DO 99 IJ=1,3

IF(IJ.EQ.1) GO TO 99

IF(IJ.EQ.2) GO TO 99

FXL2(I,J)=X(1,J)\*X(IJ,J)\*(HEATDL(IJ,1)+HEATDL(1,IJ))+FXL2(I,J)

99 CONTINUE

DO 19 J=1,NP

DO 19 I=1,NCP

FXCSHT(I,J)=0.5\*(1.0-X(I,J))\*FXL1(I,J)-0.5\*FXL2(I,J)

19 CONTINUE

C

C SH AND CH ARE LIQUID AND VAPOR ENTHALPIES RESPECTIVELY.

C THE FIRST PART OF EACH EQUATION IS A LINEAR REPRESENTATION

C OF THE IDEAL ENTHALPIES.

C

DO 74 J=1,NP

I=1

SH(I,J)=0.5279\*T(J)\*W1+FXCSHT(I,J)

CH(I,J)=SH(I,J)+224.2\*W1



```

      SH(I+1,J)=0.5996*T(J)*W2+FXCSHT(I+1,J)
      CH(I+1,J)=SH(I+1,J)+472.5*W2
      SH(I+2,J)=0.9995*T(J)*W2+FXCSHT(I+2,J)
74    CH(I+2,J)=SH(I+2,J)+947.05*W2
      DO 67 J=1,NP
      SUMY(J)=0.0
      DO 66 I=1,NCP
66    SUMY(J)=SUMY(J)+Y(I,J)
      DO 67 I=1,NCP
67    Y(I,J)=Y(I,J)/SUMY(J)
      DO 75 J=1,NP
      FV(J)=0.0
      FL(J)=0.00
      DO 75 I=1,NCP
      FV(J)=FV(J)+CH(I,J)*Y(I,J)
75    FL(J)=FL(J)+SH(I,J)*X(I,J)
      DO 51 J=1,NP
      Q(J)=0.00
      G(J)=0.0
51    HF(J)=0.0
      DO 68 J=1,NP
      DO 68 I=1,NCP
68    XF(I,J)=0.00
C
C   XF IS FEED COMPOSITION.
C
      XF(2,KK)=1.0
      XF(1,IK)=0.0718
      XF(2,IK)=0.0972
      XF(3,IK)=0.8310
      PROFL(NP)=F(KK)+F(IK)-U(1)
      PROFL(1)=FLOD*U(1)
      V(2)=PROFL(1)+U(1)
C
C   HF IS FEED ENTHALPY.
C
      DO 69 J=1,NP
      I=1
      HF(J)=0.5279*T(J)*W1*XF(I,J)
      HF(J)=HF(J)+(0.5996*T(J)*W2*XF(I+1,J))
69    HF(J)=HF(J)+(0.9995*T(J)*W2*XF(I+2,J))
      NPP=NP-1
      DO 79 J=2,NPP
      XRX=(FL(J-1)-FL(J))*PROFL(J-1)
      RXX=(FL(J)-FV(J))*(V(J)+G(J))
      RBX=(HF(J)-FL(J))*F(J)
      RRB=(FL(J)-FV(J+1))
      V(J+1)=(XRX+RXX+RBX-Q(J))/RRB
79    PROFL(J)=F(J)+PROFL(J-1)+V(J+1)-V(J)-G(J)-U(J)
      RETURN
      END

```









### \$ IBFTC Ray

Ideal enthalpies are calculated from Chao-Seader by assuming  
 $K_{ij}$  = f/p ratio for liquid phase.

1. Column pressure, psi       $P = 14.7$

2. Critical temperature      TC

Acentric factor      W

Critical pressure      PC

For every component

### \$ IBFTC Lili

$K_{ij}$  (Wilson) subroutine

1. The binary interaction energies

ALAMDA(N,L) etc.

where N = component 1

M = component 2

L = component 3

2. Parameters for the temperature dependent densities

RHO(N) etc

3. The molecular weights

$B(N) = 58.046/RHO(N)$

where B(N) is molar volume for component N.

4. System pressure, mm Hg.      TP = 760.0

5. Vapor pressure equations

VP (N,J) etc.

The parameters are those for the Antoine equation (Obtained from Lange's Handbook).



## \$ IBFTC Kathy

### New Rates Subroutine

1. Molecular weights W1, W2, W3
2. Heats of solution at infinite dilution

HEATDL(1,3) etc.

These are obtained from the critical tables.

3. Ideal enthalpy equations

liquid enthalpy

$$SH(I,J) = 0.5279 * T(J) * W1 + EXCSHT(I,J)$$

vapor enthalpy

$$CH(I,J) = SH(I,J) + 224.3 * W1$$

where 224.3 is the heat of vaporization in calories,  
gm

0.5279 is heat capacity in cal  
gm - degree F

This is repeated for each component.

4. Feed compositions

XF(3, KK) etc.

This is composition of component 3 in the solvent stage KK.

5. Feed enthalpies

The heat capacities of the components should be changed  
in the calculation of HF(J).

### Data Cards to be Changed

1. Initial profile

X01050.0152.0000.0

Format (IX, I2, 3F5.1)





Stage number     =    I2    =   01

Temperature     =   F5.1 =   050.0   °C

Liquid rate     =   F5.1 =   152.0   moles/U.T.

Vapor rate      =   F5.1 =   000.0   moles/U.T.

This is for stage 1 (Condenser) and is repeated for every stage.











**B29871**